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## CONTENTS

### SEC. A.—PHYSICAL SCIENCES

	Page
The Application to Artillery of the Photoelectric Cell Method of Measurement of Projectile Velocities— <i>D. C. Rose</i> - -	1

### SEC. B.—CHEMICAL SCIENCES

The Efficiency of Packings for Laboratory Distilling Columns— <i>Melville J. Marshall, Forestier Walker and Donald H. Baker</i> -	1
The Viscosity of Vinyl Acetate— <i>D. O. White and A. C. Cuthbertson</i>	7
Sorption of Water and Alcohol Vapors by Cellulose— <i>J. K. Russell, O. Maass and W. Boyd Campbell</i> - - - - -	13
Studies on Lignin and Related Compounds. XXVII. Methylation and Structure of Methanol Lignin (Spruce)— <i>Jack Compton and Harold Hibbert</i> - - - - -	38
Derivatives of Substituted Succinic Acids. II. The Conversion of $\alpha\alpha'$ -Diarylsuccinamides into Diarylacetic Acids— <i>John A. McRae, William R. Conn and Kenneth J. Platt</i> - -	46

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# Canadian Journal of Research

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VOL. 15, SEC. A.

JANUARY, 1937

NUMBER 1

## THE APPLICATION TO ARTILLERY OF THE PHOTOELECTRIC CELL METHOD OF MEASUREMENT OF PROJECTILE VELOCITIES<sup>1</sup>

By D. C. ROSE<sup>2</sup>

### Abstract

An outline of the method in which the projectile interrupts successively beams of light shining on photoelectric cells placed along the trajectory is given. The velocity is measured by means of records taken of the times between interruptions of the beams of light. An area about 24 by 30 in. is made sensitive to the projectile by reflecting a beam of light across this area several times, then directing it on the photoelectric cell. The details of the apparatus are given.

The recording apparatus consists of an amplifier which impresses the current pulse from the photoelectric cell on the grid of a thyatron when the projectile interrupts the light beam. This thyatron, on discharging a condenser, emits a short flash of light which is recorded on a rotating drum camera. A similar thyatron controlled by a tuning fork puts a simultaneous time record on the film. The camera is so designed that the film can be taken out and developed in daylight.

The results of firing tests in Petawawa indicate that the apparatus can be used successfully in daylight with field guns. The present equipment measures velocities with a probable error of less than 2 ft. per sec. for muzzle velocities of the order of 1600 ft. per sec. Improvements in design are discussed.

### Introduction

The method of measuring the velocity of projectiles which was developed recently in the National Research Laboratories, Ottawa, has been applied to artillery and was tried successfully with a field gun. The method is described in detail elsewhere (1, 2) with its application to rifle bullets, and is outlined briefly as follows. The projectile interrupts successively beams of light shining on photoelectric cells. The current pulse in the photoelectric cell caused by the interruption of the beam of light by the projectile, after suitable amplification, is recorded photographically. A time record is also imposed on the photographic record, so that the time of flight of the projectile between successive beams of light can be measured and hence its velocity calculated.

For the present experiments a considerable part of the equipment was redesigned to make it semiportable. Some alterations were made necessary by the fact that it had to be used at a firing point unequipped with electric power. Hence much of the apparatus will be described in detail so that continued reference to previous reports will not be necessary.

<sup>1</sup> Manuscript received December 2, 1936.

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### Lamp and Photoelectric Cell Frames

Experience with rifle bullets indicated that good results should be obtained, in the case of a field gun, with the beams of light about 20 ft. or more apart. Actually, as the results will show, one of the greatest sources of error is in the measurement of the distance between the beams of light, because of the difficulty in locating the edge or centre of a beam of light that is not sharply defined. Obviously, greater distances apart lead to greater accuracy and ease of measurement, but practical considerations led to the choice of a distance of about 50 ft. between the light beams. Four photoelectric cell and lamp stations were used. These will be numbered Stations 1, 2, 3, and 4. Station 1 was situated about 65 ft. from the muzzle, and the others were at intervals of approximately 50 ft. along the trajectory. Only three sets of photoelectric cell and lamp equipment were constructed, so that only three of the four stations could be used at once.

Consideration of jump, errors in laying, etc., made it advisable to construct the lamp and photoelectric cell equipment in such a manner that a rectangular area about 24 by 30 in. at right angles to the trajectory would be sensitive for recording purposes. This was done by reflecting a beam of light back and forth several times between two mirrors, as shown in Fig. 1. The beams of

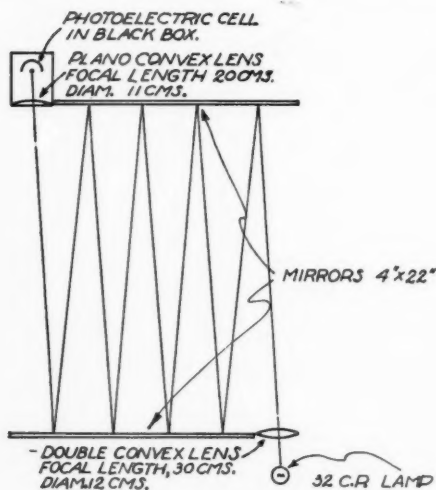


FIG. 1. Arrangement of light beam.

light were about four inches in diameter, and were reflected back and forth in such a manner that there were no blind areas in a central rectangular region of approximately 24 by 30 in. The mirrors, the lamp and the photoelectric cell boxes were supported on light but rigid angle iron frames whose outside dimensions were 4 by 2 $\frac{3}{4}$  ft.

The projector consisted of a 32 c.p., six-volt automobile headlight bulb and a single condensing lens having a focal length of about 30 cm. and a diameter of 12 cm. This simple arrangement did not give as well defined a beam of light as might be desired. However, as the present experiments

were only of a preliminary nature to test the practicability of the equipment for field guns, it was not considered advisable, at present, to make further refinements on the optical system to improve the light beams. In a permanent set-up a more elaborate optical system could be designed that would give a narrower and sharply defined light beam so that its position could be located with precision.

The lamp and mirror supports were made adjustable to facilitate focusing. The lamp was housed in a box to keep stray light from the mirrors, and the photoelectric cell was housed in a reasonably light-tight box painted black on the inside. No other precautions were taken to keep daylight from the photoelectric cell, as the lens was such that very little light except from the mirror could reach the sensitive part of the cell. The cell box was placed on the top end of the frame with the lens downward so that any stray light entering it would be only that scattered from the ground. Stray light, that did not change suddenly and was not so intense that it affected the sensitivity of the photoelectric cell, would be expected not to affect the recording equipment, because only short-period pulses in the photoelectric cell current were amplified, and a steady or slowly varying small current in the cell circuit caused by stray light would not affect the recording circuit. Actually the photoelectric current caused by stray light and insulation leakage was often of the same magnitude as the current due to the light from the lamp, but though the apparatus was used both in bright sunlight and under cloudy conditions, and with clouds moving over the sun, no trouble was experienced by the effects of these stray currents.

To allow for photoelectric cells of different sensitivities and for different efficiencies of the lamp, the lamps were controlled by individual rheostats and the current adjusted so that approximately the same photoelectric current flowed in each. General Electric PJ-22 photoelectric cells were used with a series coupling resistance of one megohm and 90 volts on the anode. The light intensity employed was such that approximately 2 microamperes flowed in each cell.

#### *Method of Recording*

#### **Recording Apparatus**

In previous experiments (1, 2), three general methods of recording were used. In the first method, the photoelectric cell current, after amplification with a d-c. amplifier, was measured by means of an Einthoven galvanometer and recorded photographically. This method was discarded immediately because the arrangement was too sensitive to disturbances, and the Einthoven galvanometer had too long a natural period. In the second method, the amplified pulse of the current produced when the projectile interrupted the beam of light was impressed on the grid or control electrode of a thyratron in such a way that the thyratron discharged a condenser; the discharging current was recorded by the Einthoven galvanometer. An a-c. amplifier was used in this case. This method gave satisfactory results, but was improved considerably in the third experiment in which the Einthoven galvanometer was eliminated, and a photographic record was made of the flash of light emitted by the thyratron when it discharged a condenser. Another thyratron that was controlled by an electrically driven tuning fork and that emitted either 500 or 1000 flashes per second produced the time marks on the photographic film.

Fig. 2 shows a schematic arrangement of the new recording equipment used in the present investigation. The amplifier controls thyatron *A* in such a manner that each time a beam of light is interrupted by the projectile the thyatron discharges a condenser and emits a very short flash of light. (The

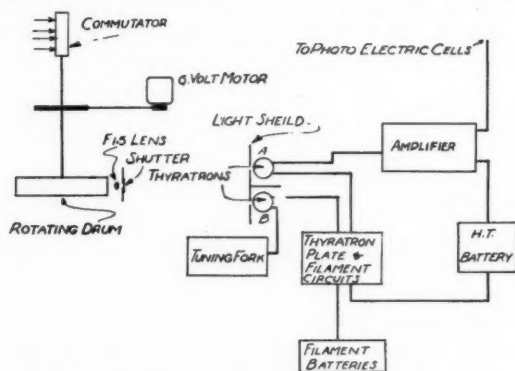


FIG. 2. Schematic arrangement of recording equipment.

flash lasts for only a few microseconds, probably less than five.) Thyatron *B* produced the time marks. These flashes of light are recorded on a rotating drum camera placed in front of the thyratrons as shown. A narrow slit directly in front of the camera defines the beam of light, and the lens forms an image of this slit on the film. A commutator driven on the same axis as the camera shutter is opened; both operations are done electrically.

### The Camera

The design of the new camera incorporated several improvements over that used with rifle bullets. The film (motion picture) was carried on a drum about 10 in. in diameter which rotated at the required speed and was driven by a six-volt d-c. motor. A diagram demonstrating the essential features is shown in Fig. 3. The camera was so designed that the whole process of taking the records, developing them, etc., could be carried out in daylight; the only process that required a dark room was the loading of the film spool. This spool carried about 125 ft. of film or enough for about 40 rounds. The film spool was light-tight so it could be mounted in the camera in daylight. Hence, by duplicating film spools, the apparatus could be used indefinitely without recourse to a dark room.

When in operation the film spool was carried inside the rotating drum and coaxial with it. The film was fed from the spool through a set of driving sprockets around the drum and over another driving sprocket, so that it could be wound off the drum through a narrow slit in the back of the camera. This slit opened into a dark box containing the developing tank, etc. To take an exposed record off the drum and to reload the camera, the rotating

drum was clamped, the gears attached to a crank were engaged with the gears driving the film sprockets, and the length of exposed film was wound off the drum into the dark box at the back of the camera. The film was then cut off with a knife that was attached to the slit, and the camera was ready for another exposure.

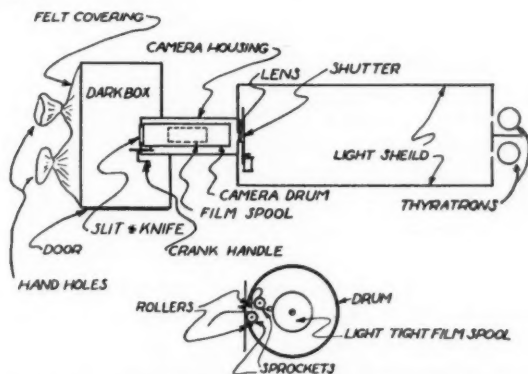


FIG. 3. Schematic diagram showing essential features of camera.

The part of the camera carrying the slit, knife and gears, was hinged so that it could be moved back from the drum to clear the gears, etc. The knife acted as a cover for the slit so that the dark box could be opened and the developing tank could be removed or inserted without causing fogging of the film on the drum. The loading of the exposed film into the developing tank was done by hand in the dark box. The hands were inserted through sleeve holes in the back of the box. The developing solution was not, as a rule, poured into the tank until the film was inserted and the tank removed from the dark box. The process of preparing the camera for another exposure and placing the film in the tank ready for development could be carried out in two minutes or less, so that with the present apparatus firing could be carried on at approximately that interval. To develop, fix and wash the film in such a way that a rough estimate of the velocity, say to about 20 ft. per sec., could be obtained, required about 15 min. For accurate measurement, a traveling microscope or an equivalent instrument must be used.

During the course of the tests at Petawawa, no dark room was used at all as sufficient film was wound on one spool for the tests, and development, etc., was carried on in daylight, sometimes almost in direct sunlight.

The apparatus could, of course, be made much more automatic. In fact, before it was built, preliminary designs were made of a much more elaborate camera in which the exposed film was automatically wound into a developing tank containing developer; then the film was washed and fixed, and it emerged from the apparatus ready for drying and measurement. If the velocity measurements were not required immediately, the exposed films could be marked and stored in the dark box and developed after the shooting was over.

The developing tank, made of Monel metal had a removable lid and contained a flat bakelite spool. Spiral grooves were cut in the end plates of the spool so the film could be fed into these grooves and so held by its edges that its surfaces were not in contact. A pouring funnel and air vent, both made light-tight, made it possible to pour the chemicals in and out of the tank in daylight.

The lens used on the camera was a Dalmeyer F 1.5 with a focal length of one inch. This lens produced on the film an image of the slit in front of the thyatron. In the apparatus used with rifle bullets a cylindrical lens was used which focused a line image of the slit in front of the thyatron. The record made with the Dalmeyer lens was much sharper and led to easier reading of the record with the microscope. Since the record consists of short lines with sharp edges fading to nothing at their ends instead of uniform lines as in the records obtained by the previous apparatus, they are not so easily reproducible and cannot be examined so readily by the eye. The lens used in the present experiment had more light-gathering power than the cylindrical lens used previously. The slit in the shield in front of the thyatron was about  $\frac{1}{4}$  in. wide and was placed 30 in. from the lens, so that the spots on the record were approximately  $1/120$  in. wide and about  $1/32$  to  $3/64$  in. long.

The shutter consisted of a rotating sector placed in front of the lens. To open and close the aperture, the sector was so designed that it rotated through about two-thirds of a revolution. The sector was driven by a spring, and the time of exposure was controlled by air damping in a dashpot. The piston was connected to the sector by a crank arm so that the motion of the sector during opening and closing would be very rapid, the control being exerted around the centre of the stroke while the shutter was open. The shutter was released electromagnetically and controlled by the commutator indicated in Fig. 2.

#### *Amplifier, Photoelectric Cell, Thyatron and Tuning Fork Circuits*

The amplifier was of the resistance capacity coupled type having a high gain. A rough measure of the gain gave a maximum voltage ratio of about 10,000, the circuit being designed for voltage amplification only, not for power output. The circuit diagram is shown in Fig. 4. The only feature worth special note in this circuit is that all the tubes were carefully decoupled from the high tension batteries with 25,000-ohm resistances and two microfarads condensers as shown. The reason for special care in decoupling was that the batteries which fed the amplifier were also used to feed the thyatron plates, and when the thyatron discharges the condenser producing the flash of light for the record, sudden loads are put on the battery which would react on the amplifier unless care were taken in decoupling. The thyatron plate circuits were decoupled from the battery as will be described later. The photoelectric cells were connected to the amplifier as shown, so that a sudden decrease in photoelectric cell current caused a positive voltage pulse on the grid. Actually only about one-quarter of the gain of the amplifier was needed. If the gain was set too high, the apparatus was subject to inter-

ference which will be discussed later; if set too low one or more of the stations might fail to produce a record. The choice of the input condenser (0.001 mfd., Fig. 4) is important in this apparatus. In the apparatus used with rifles in the basement of the National Research Laboratory in Ottawa, a

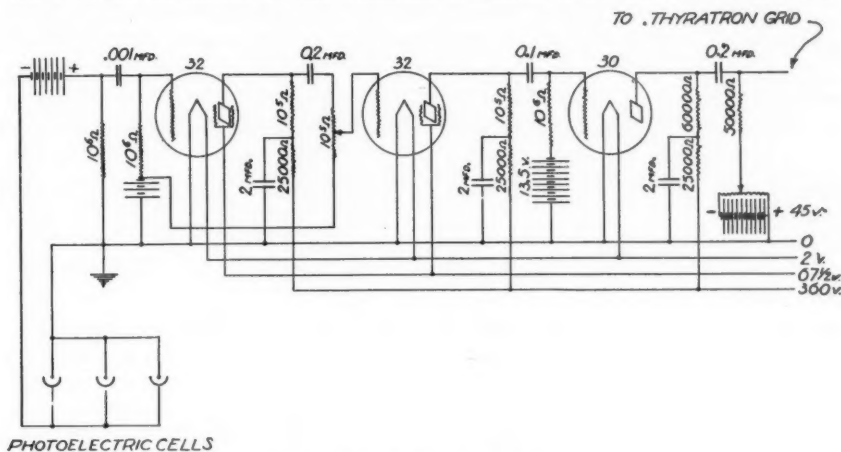


FIG. 4. Circuit diagram of amplifier.

considerable amount of trouble was experienced owing largely to vibrations in the lamp and photoelectric cell frames caused by the muzzle blast. A great deal of this was eliminated by choosing an input condenser so small in capacity that the low frequency pulses did not pass the condenser, while the short pulse caused by the bullet would be transmitted to the grid of the first tube with negligible attenuation. In the present case a condenser of 0.001 mfd. was chosen as about the smallest practicable capacity.

When the apparatus was first set up at Petawawa considerable interference was experienced which is believed to be due to atmospherics. The wires connecting the amplifier with the photoelectric cells were hung overhead on trees and posts. As local thunderstorms were numerous and the amplifier is very sensitive, it was not entirely unexpected that some atmospherics should be picked up. However, this trouble was eliminated by burying the wires underground or pegging them down to the surface of the ground.

Fig. 5 shows a circuit diagram for the plates and filament circuits of the thyratrons. The filaments, requiring 2.5 volts each, were connected in series for the sake of convenience so that they could be fed from a six-volt battery. To compensate for slight differences in the filament resistances a small rheostat not shown in the figure was connected across the filament of higher resistance, so that the required 2.5 volts could be kept correct across both filaments. A jack (not shown) for a voltmeter to check the voltage completes the filament circuit. The plate circuit was decoupled from the batteries as shown. When the positive pulse from the tuning fork or amplifier is impressed on the grids,

the 0.5 mfd. condensers discharge through the thyatron concerned and the condenser starts to recharge immediately through the resistance  $A$ , the drop in it being sufficient to extinguish the arc in the thyatron. The decoupling condensers and resistance (5 mfd. and 1,000 ohms) smooth out the battery current required to recharge the condenser, so there is no effective reaction on the amplifier fed from the same battery.

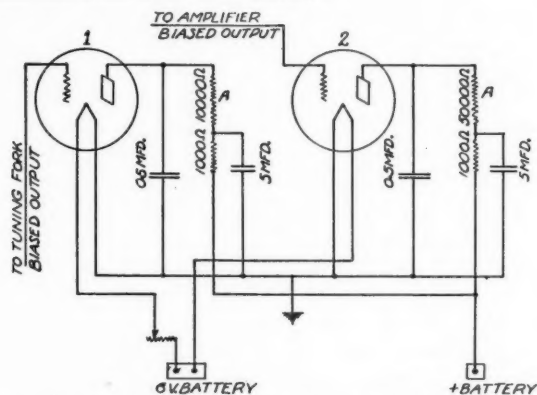


FIG. 5. Circuit diagram for the thyatrons. 1. Time marker controlled by tuning fork. 2. Controlled by photo electric cells.

Thyatron of a commercial type, namely, General Electric FG-17, were used with this equipment. Unfortunately, the General Electric Company has changed some structural details of this tube recently, making it unsuitable for this type of recording. The control electrode in the older type which was used here consisted of a cylinder made from perforated sheet metal so that considerable light was emitted. In the new type the control electrode is constructed from plain sheet metal, the result being that except for that from a small hole virtually no light is emitted. This small hole would give sufficient light for a good readable record if less reduction in the size of its image on the film were used, but would not be as satisfactory as the slit used in the present arrangement. However, the FG-17 is not the only tube having suitable electrical characteristics. A more suitable tube has been built specially for the purpose by the writer (3), but as it is not a commercial product, it was not used. There are other commercial tubes that would work very well; for instance, an open type rectifier tube might be used in series with a thyatron. This has the disadvantage that extra insulated filament batteries would be required. Probably the most suitable commercial tube would be one similar to that used with the Westinghouse Strologlow equipment No. KU-610, though this has not been tried, nor have the possibilities of other commercial products been investigated. There is, however, not the slightest doubt that a commercial tube as efficient as the FG-17 for the required purpose could be found easily, and it has been shown definitely that very satisfactory tubes can be constructed.

The tuning fork equipment was of a standard type manufactured by the Cambridge Instrument Company. It consisted of a 1,000-cycle steel tuning fork maintained in vibration electromagnetically by a circuit involving a vacuum tube, so that no mechanical contacts are required on the vibrating fork. The circuit details are not given as it is a standard manufactured product. The circuit includes an output transformer in order that an alternating voltage of about two volts may be obtained from the fork. An impedance matching transformer with tapped secondary was inserted in the circuit so that a slightly higher voltage could be impressed on the grid of the thyratron. The tuning fork, a 45-volt biasing battery and a potentiometer were enclosed in a metal box in order that the electric fields generated in the tuning fork circuit would be shielded from the amplifier.

The tuning fork was calibrated some time before it was used in Petawawa, and a recalibration was made shortly after it was returned to Ottawa. Its frequency was found to be  $995.9 \pm 0.1$  cycles per second. The calibration was made by comparing it with the radio frequency standards belonging to the Canadian Broadcasting Corporation. The accuracy of these standards is known to one part in ten million.

#### *Commutator and Firing Circuits*

As was mentioned previously, it was essential that the firing of the gun and the tripping of the shutter take place in proper sequence so that the record would appear in the correct place on the film. To ensure this an electrically controlled mechanical firing mechanism was built, which will be described in the next paragraphs. The position of the contacts on the commutator had to be adjusted ahead of the actual time of the beginning of the exposure to compensate, for the lag in the shutter, for the time taken for the firing mechanism to fire the gun, and for the time taken for the shell to approach the first photoelectric cell station. The lag in the shutter was easy to adjust experimentally by running the camera at the correct speed, taking exposures, making adjustments on the commutator and shutting the dashpot until the record appeared in the correct position on the film. Once the shutter adjustments on the commutator and dashpot were made they did not have to be reset unless wide variations in camera speed were used. The time between the firing of the gun and the shell reaching the first station could be calculated with sufficient accuracy, for the purpose, from the approximate velocity of the projectile and the known distances involved, but the time lag in the firing mechanism had to be measured. This was done by inserting an insulated electrical contact in place of the cap in a used cartridge, and using the contact made on this by the firing pin to control the thyratron which would normally be controlled by the photoelectric cells. The gun time lag was found to be much greater than the shutter time lag, hence the firing contacts on the commutator had to be made first. The correct time lags were set on the commutator before the apparatus was shipped to Petawawa, and when the actual firing was carried out it was found that no further adjustment was necessary as the first records appeared on the correct

portion of the film. On the last day of firing when the distances of the photo-electric cell stations were increased beyond that for which the original time lags were calculated, the gun firing contacts were set slightly forward though the position of the record on the film was such that this was not necessary.

The electrical circuit controlling the shutter and firing mechanism is shown in Fig. 6. In operating the apparatus, the operator has no way of knowing whether he closes the switch before the firing contacts close or between the

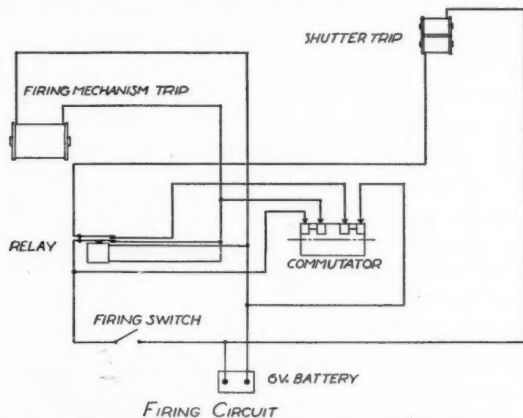


FIG. 6. Circuit diagram for electrically controlled shutter and firing mechanism.

times at which the gun contacts and the shutter contacts are closed. If it should be the latter case the shutter would be tripped and the exposure made before the gun was fired, so no record would be obtained. In order to avoid this, some auxiliary equipment had to be introduced to prevent the shutter from operating until after the firing circuit was completed. This was done by introducing into the circuit a relay whose winding was in parallel with the firing trip coil. The relay has two separate contacts on its armature, one of which is merely a holding circuit, so it will stay closed, once it is energized, during the time that the firing switch is closed, and the other contact controls the battery power on the shutter coil and shutter contacts on the commutator.

#### *Firing Mechanism*

In order to avoid the necessity of any alterations to the usual firing mechanism on the gun, it was decided that the electrically controlled auxiliary firing mechanism should be so constructed that it would pull the firing handle in the usual way. Further, such a firing mechanism could be adapted easily to fire other types of guns in common use. Hence, a spring driven mechanical firing mechanism was designed which could be released electrically and which would exert enough pressure to fire the gun easily. A schematic diagram of the arrangement of the various links used to transmit the spring tension to the firing handle is shown in Fig. 7. To apply a straight spring directly to

the firing handle would have necessitated the use of a very long spring. Further, the maximum force is required near the end of the stroke rather than at the beginning. Hence the arrangement of the spring and connecting links was made such that at the beginning of the stroke the mechanical advantage between the spring and the link pulling the firing handle was about 0.3, or the force applied at the beginning of the stroke was 0.3 times the spring force when the mechanism was in the fully cocked position (the schematic drawing shows it in the cocked position). On the other hand, at the end of the stroke the ratio was 1 : 1, so that the full force of the spring was exerted on the firing handle. The spring unit consisted of 12 Ford valve springs, two parallel banks of six in series. A calibration of a sample spring showed that the total

force exerted by the unit at full cock was about 164 lb., while in the uncocked position the force was about 82 lb. If friction is neglected, and the mechanical advantages mentioned above are used, this indicates that a static force in the firing handle varying from about 50 lb., at full cock, to about 82 lb. at the end of the firing stroke was available. The apparatus possessed the necessary reserve power to cock and fire the gun mechanism. The time lag between the closing of the firing circuit contacts on the commutator and the firing pin striking the cartridge was very close to  $\frac{1}{10}$  sec., three separate measurements differing by not more than 6%. The magnetic trip consisted of two links as shown. The final trigger at *A* (Fig. 7) was a roller, so that a very small magnetic pull, probably less than an ounce, would trip the whole mechanism.

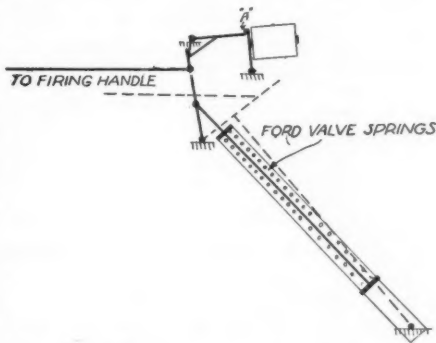


FIG. 7. Schematic diagram showing electrically controlled firing mechanism.

#### *Results of Firing Trials*

The apparatus was taken from Ottawa to Petawawa on July 22, 1935, and was set up at a convenient range in the vicinity of the military camp. By the afternoon of July 24 various troubles, such as interference due to atmospherics, had been eliminated, and the apparatus was ready for firing. Four rounds were fired on July 24. The first round was used to verify the jump calculations by firing through paper screens instead of the lamp and photoelectric cell frames. It also served to test the firing apparatus. Jump calculations proved to be correct, so the frames were mounted in position. For Rounds 2, 3 and 4 only two lamp- and photoelectric-cell stations were used, namely, 2 and 3. The results of all firing are summarized in Table I. On the following day four more rounds were fired, using Stations 1, 2 and 3, and various settings of the gain control on the amplifier. With about 18 to 20%

#### **Results**

of the gain of the amplifier, the record showed the three flashes of light which were identifiable as being due to the three photoelectric-cell stations, but there were also three other flashes probably due to the effect of the muzzle blast in causing the first lamp frame to vibrate. With a reduced gain, about 13%,

TABLE I  
RESULTS ROUND BY ROUND

Round	Velocity in feet per sec.		
	Station 1 and 2	Station 2 and 3	Station 3 and 4
1	Trial round with paper screens.		
2			
3	No record (shutter improperly set).		
4			
5	1592	1586	
6	1596	1587	
7	No record (amplifier setting too insensitive).		
8			
9		1592	
10		1609	1598
11		1595	1600
12		1610	1602
13		1596	1588
14		1606	1598
15		1593	1589
16		1589	1585
			1590

the interference was reduced to one flash, though again a good velocity measure could be made. With the gain reduced to about 9% only one station recorded. Hence with the equipment used, the limit, between a record showing the three desired flashes with no interference and such a reduced sensitivity that no record was obtained, was too small to be practicable. In the present case the interference attributable to the muzzle blast had no detrimental effect on the actual measure of the velocity, as it does not occur at nearly the instant that the shell is passing through one of the light beams. However, with different velocities this interference might be serious. To overcome it two alternative procedures were available: First, by a change in the structure of the first lamp and photoelectric cell frame, such as increasing its rigidity and using more intense light beams, or, secondly, the use of photoelectric cell stations at greater distances from the muzzle. The first alternative was not practicable in the present case without considerable machine shop work, and as it was desirable to obtain as perfect a record as possible with little delay, the second alternative was tried. On the following day, July 26, a fourth lamp and photoelectric cell station was set up about 50 ft. beyond Station 3, and the equipment at Station 1 was moved to Station 4. With Stations 2,

TABLE II

Measured distance	Feet
Muzzle to Station 1	66.07
Muzzle to Station 2	117.11
Station 1 to Station 2	51.04
Station 2 to Station 3	49.68
Station 3 to Station 4	52.35

3 and 4 in operation and the amplifier set at about 20% of full gain, eight rounds were fired. A good record was obtained for each round except the last, when for some unaccountable reason Station 2 failed to record.

The distances from the muzzle and between the various stations are given in Table II.

In the case of Round 3 no record was obtained because of a misadjustment in cocking the camera shutter. In all other cases except Round 16 a complete record was obtained as expected, and except for Round 10 a reasonable measure of the velocity was obtained in every case. In the case of Round 10, owing perhaps to some interference occurring almost at a time when the shell was passing a light beam, an improbable result was obtained, in that the shell appeared to increase in velocity as it moved farther from the gun. The exact reason for this result remains unknown, and this round has been omitted in all further discussion. A reversed print from the record of Round 15 is shown in Fig. 8.

#### Accuracy

A full discussion of the sources of error with the type of apparatus used in this experiment is given in a previous paper (1). The sources of error which may affect the results are in the measurement of records and in the location of the point where the shell interrupts the beam of light. Errors in measurement of the record can be neglected, as the distances between the marks on the film could be measured to  $\frac{1}{80}$  mm., which corresponds to a velocity error of about 0.3 ft. per sec. The second source of error is much more important, that is, in measuring the distance between photoelectric-cell stations. This is due to the fact that the optical system used did not define the beam of light with sufficient accuracy. The distance between stations was measured from corresponding points on the steel frames supporting the lamps, photoelectric cells and mirrors. This distance could be measured to about  $\frac{1}{8}$  in. which would represent a negligible error in velocity. The optical parts at each station were made similar, but the point where the nose of the shell interrupted sufficient light to cause the thyatron to function might vary from round to round or station to station by as much as  $1\frac{1}{2}$  to 2 in. owing to the fact that the beam of light was more or less circular in cross section. An error of two inches in the distance between stations represents an error in velocity of about 5 ft. per sec. As was

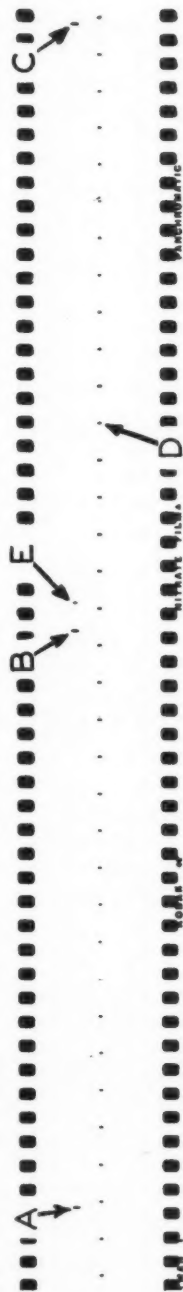


FIG. 8. Record for Round 15. A. Station 2. B. Station 3. C. Station 4. D. Time marks, 467.9 per sec. E. This flash occurs occasionally because of the relatively long period of recovery of the amplifier after an intense pulse. It is easily recognized from the period following the previous flash which is a characteristic of the thyatron circuit. It does not affect the result.

mentioned previously, this error could be reduced considerably by redesigning the projection apparatus. This would be comparatively easy if electric power were available at the firing point where trials were being made, as a narrow well defined beam of light could be produced by using a longer focus projecting lens and a more intense source. With the present apparatus the power had to be furnished by storage batteries, and as the apparatus had to be made portable it was necessary to limit the number of batteries carried to a minimum. Further, standard makes and easily replaceable lamps, lenses, etc., were used throughout. There is no doubt that, with a little further investigation at perhaps but slightly greater expense, new projection equipment could be constructed which would reduce the maximum error due to this uncertainty to 1 or 2 ft. per sec. for distances between stations of 50 ft. Of course, if greater distances were used the error would be proportionately lower. Actually, the mean difference between velocities in Columns 3 and 4, Table I, for the last eight rounds (except Round 10) is 7.2 ft. per sec. The mean deviation of this difference from the mean difference is 2.1 ft. per sec. Hence from these observations the probable error is of the order of 2 ft. per sec., though too few rounds have been fired for a reliable estimate.

### General Conclusions

The results described in this report indicate that the photoelectric cell method for measuring projectiles is easily applicable to artillery. The equipment is not affected by daylight and the first observing station can be located as close as 100 ft. from the muzzle, for the gun used for these trials. With more rigid structures this distance could probably be made considerably shorter. The apparatus could be made portable in that it could be mounted on a truck and be ready for operation as quickly as supports for the lamp and photoelectric cell frames could be mounted. However, except in special gun positions where low trajectories of 200 ft. or so can be used, this might involve considerable structural work. Further, if electrical power were available several simplifications in design and operation could be made.

### Acknowledgments

These experiments were carried out with the collaboration of Major G. P. Morrison, R.C.A., and their success is due to his enthusiasm and numerous contributions to the design and operational details. The thanks of the writer are also due to the Camp Commandant, Petawawa, for providing facilities and men to carry out the tests in Petawawa, and to the O.M.E.C.C. for structural details and for repairs made in the Ordnance workshop in Petawawa.

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## THE EFFICIENCY OF PACKINGS FOR LABORATORY DISTILLING COLUMNS<sup>1</sup>

By MELVILLE J. MARSHALL<sup>2</sup>, FORESTIER WALKER<sup>3</sup>, AND DONALD H. BAKER<sup>4</sup>

### Abstract

The efficiency of jack chain packings, with alcohol-water mixtures, increases by only 13.2% with decrease in the size of the chain links from No. 18 to No. 22, while a drop in capacity of 36.7% is noted. If all factors are taken into consideration, No. 18 jack chain is the most desirable of those studied. The efficiency of Lessing rings, 0.22 in. in diameter, is higher than that of any of the chains studied, but the capacity is much less than that of No. 18 chain, and only slightly better than that of No. 22 chain.

### Introduction

The use in recent years of small packed distilling columns for laboratory distillation has resulted in the introduction of a number of very efficient packing materials. Of these various packings, jack chain is often preferred because of the facility with which it can be handled. However, little use has been made of sizes smaller than No. 18, although it is known that a decrease in size results in a higher efficiency. In the present investigation the writers studied the effect of chain size on the efficiency and capacity of the packing, in order to determine the possibility of utilizing the smaller chain sizes to advantage.

### Theory

Peters (6) was the first to calculate the number of perfect plates in a packed column. He used an equation similar to that of Lewis (3; 8, p. 600), as follows:

$$x_{n+1} = \frac{y_n - (1 - O/V)x_e}{O/V},$$

where  $x_{n+1}$  is the mole fraction of the more volatile component in the liquid on the  $n + 1$ th plate,  $y_n$  is the mole fraction of the more volatile component in the vapor from the  $n$ th plate,  $x_e$  is the mole fraction of the more volatile component in the distillate,  $P$  is the number of moles of distillate withdrawn as product per unit time,  $O$  is the overflow from one plate to another down the column in moles per unit time,  $V$  is the number of moles of vapor per unit time passing up the column,  $O/V$  is called the reflux ratio.

<sup>1</sup> Original manuscript received September 8, 1936.

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By dividing the height of the column by the calculated number of perfect plates, Peters (6) obtained a value characteristic of the efficiency of the column, which he called "the height equivalent to a perfect plate" or the H.E.T.P. As the efficiency is really inversely proportional to such a number, it would be preferable to define the efficiency as the number of plates per foot or per metre.

The efficiency is not the only criterion of the desirability of a given packing. The capacity of the packing to carry an adequate flow of vapor up the column without flooding is almost of equal importance. It is evident that the maximum reflux ratio permissible for a given amount of product per unit time decreases with decrease in the capacity of the packing. This, in turn, means a decrease in separating power, as can be seen from the equation. It is important, therefore, to employ packings that possess the highest combined capacity and efficiency.

The capacity is usually measured in terms of the maximum volume of vapor per unit time passing unit cross section of the column without flooding. This quantity has the dimensions of a velocity, and is called the maximum vapor velocity. Peters (6) found, experimentally, that this maximum vapor velocity dropped off as a linear function of the reflux ratio, giving a minimum value at total reflux. In the present investigation the capacity of a packing is defined as the maximum vapor velocity attained at total reflux.

### Experimental Details

For comparison with previous work done in this laboratory, a mixture of ethyl alcohol and water was chosen to test the column. Care was taken to prevent the composition of the distillate approaching too closely that of the constant boiling mixture, as the theoretical change in concentration per plate is very small in this region.

The experimental column, shown in Fig. 1, was constructed entirely of Pyrex glass, and was modeled somewhat after the laboratory column previously described by the senior writer (4). The boiling flask, G, was covered with asbestos cement to prevent undue heat loss. Heat was introduced by passing direct current through a nichrome wire immersed directly in the liquid. The rate of energy dissipation was measured in watts by means of an ammeter and a voltmeter. To obtain the amount of heat actually entering the column, the power in watts necessary to barely distil liquid out of the flask without the column was determined. This value was found to be 36

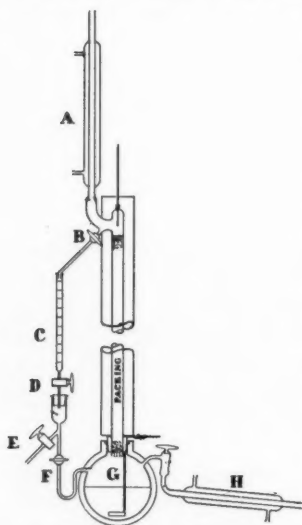


FIG 1. Experimental column.

watts or 8.6 cal. per second. The amount of energy entering the column per second with the vapor was obtained by subtracting this amount from the total power dissipated in the still. When converted to moles per second, this gives the vapor velocity,  $V$ .

The internal diameter of the column proper was 2.2 cm., and it was filled with packing to a height of 100 cm. It was heat insulated with steam pipe insulation, and correction was made for any possible heat loss by passing a current through a nichrome winding between the insulation and the glass column. Preliminary tests were made with no reflux down the column, and 40 watts was found to be necessary to just prevent condensation on the column walls. This value was verified by calculation of heat losses from the mean temperature difference and the conductivity of the insulation.

All the vapor passing the column was condensed in the reflux condenser, *A*. By adjustment of the glass stopcock *B* part of this reflux was passed back down the column and part was run into the burette, *C*. The rate at which the burette filled with product was determined by means of a stop watch. The condensate was then passed back to the boiling flask by opening stopcock *D*. A sample of the product was withdrawn for each run by closing stopcock *F* and opening *E*. A sample of the vapor in the boiling flask was withdrawn through the condenser *H*. The density of each of these samples was determined by means of a pycnometer, after which the samples were returned to the still. From these values the composition of the vapor entering, and that of the vapor leaving, the column were determined by reference to the density tables in the Smithsonian Physical Tables (6th ed.).

To obtain values for the capacity of the packings, the column was run at total reflux, and the heat input just necessary to cause flooding was determined. From the molal heat of vaporization the number of cubic centimetres of vapor at normal temperature and pressure passing unit cross section of the column could be obtained as a velocity in centimetres per second. The medium for most of these tests was alcohol (95% by weight), so the values obtained are practically those for the constant boiling mixture. In addition, some measurements were made with water, and some with alcohol and water mixtures of the same composition as those used in the efficiency determinations.

## Results

The efficiency determinations for 0.22 in. Lessing rings, and Nos. 18, 20, and 22 single link brass jack chain are given in Table I. The method of calculation was exactly the same as that described by Marshall and Sutherland (5).

Table II contains the averages of the H.E.T.P. values of Table I, and the capacity of each packing expressed as a maximum vapor velocity. The maximum heat input at total reflux is included for comparison with the heat input data of Table I.

TABLE I  
EFFICIENCY DETERMINATIONS

Reflux ratio	Heat input, watts	H.E.T.P., cm.
<i>Lessing rings</i>		
0.670	404	10.2
.812	408	10.0
.815	291	11.2
.816	388	11.1
.839	404	10.0
.857	360	10.0
.868	372	10.6
.868	170	10.0
<i>No. 18 Single link jack chain</i>		
0.802	294	12.0
.773	294	13.5
.805	404	14.0
.553	276	12.5
.841	353	13.0
.933	494	11.8
.860	386	12.5
.890	438	13.5
<i>No. 20 Single link jack chain</i>		
0.897	420	13.2
.854	360	11.3
.954	416	13.8
.818	281	13.1
.910	405	10.6
.894	364	12.5
.860	388	13.6
.843	440	13.8
.803	280	13.3
<i>No. 22 Single link jack chain</i>		
0.850	365	11.4
.855	360	11.9
.932	492	11.8
.900	403	10.6

A determination of the capacity of No. 18 chain, using water as the medium, gave a value of 215.2 cm. per sec. This very high value is due largely to the very small molecular volume of the liquid water. Similar determinations with No. 18 and No. 20 chains, using 15% alcohol in the still, which is about the concentration used in obtaining the efficiencies, gave results approximately 5% higher than those for 95% alcohol. This is explained by the fact that, at total reflux, the alcohol concentration at the top of the column is greater than 90%, even when that in the boiling flask is as low as 15%. As the capacity of the packing varies throughout the length of the column owing to variation in the composition of the reflux, it is evident that the capacity of the column as a whole is limited to the minimum capacity anywhere in the column.

The capacity of a column is also limited by the size of the condenser employed. In the present work, an ordinary Liebig condenser, made by the Corning Glass Co., was found to flood at 598 watts. To handle the highest rates of distillation it was necessary to replace the Liebig condenser with one of larger internal diameter. This point should be given some consideration when reflux columns for general laboratory purposes are designed.

TABLE II  
AVERAGES OF H.E.T.P. VALUES OF TABLE I, AND CAPACITY OF EACH PACKING

Packing	H.E.T.P., cm.	Plates per metre	Max. heat input at total reflux, watts	Max. vapor velocity, cm./sec., 95% alcohol
No. 18 chain	12.9	7.75	709	104.5
No. 20 chain	12.8	7.81	667	98.3
No. 22 chain	11.4	8.77	449	66.2
Lessing rings	10.4	9.62	465	68.6

It is evident from Table II that no great gain in efficiency can be attained by decreasing the size of the chain from No. 18 to No. 22. Since a link of the No. 18 chain measures 6.3 mm. in width, compared with only 3.3 mm. for the No. 22 chain, the writers expected a greater increase in efficiency than was actually obtained. This small increase in efficiency, in view of the much larger decrease in capacity, the greater weight in the column, and the higher cost of No. 22 chain, hardly justifies the use of this chain for ordinary distillation. There seems to be no great advantage in using No. 20 chain, in view of the larger capacity of No. 18 chain and the small difference in their efficiencies. It would appear, then, that No. 18 chain is the most generally desirable of the three sizes. It is very probable, however, that a chain much lighter in construction than the conventional jack chain would give higher efficiencies in the smaller sizes.

No other efficiency values, with alcohol-water mixtures, are available for chain packings. For other mixtures, a number of values for the larger chain sizes can be found in the literature, particularly for benzene-carbon tetrachloride mixtures. No relative capacity measurements are available. Fenske, Quiggle and Tongberg (1, 2) have measured the efficiencies of chains from No. 16 to 20, but as these measurements have been distributed among a number of columns and mixtures, it has been found impossible, particularly in the absence of capacity data, to apply their results to the present problem. It is interesting to note, however, that the present efficiency values with alcohol-water mixtures are very close to their corresponding values with benzene-carbon tetrachloride and heptane-toluene mixtures, although in general the efficiency is found to vary with the nature of the mixture.

### Comparison with Other Packings

Fewer data are available in the literature for capacity than for efficiency. Peters (6), calling the capacity of 0.25 in. hollow cylinders 100, estimated that the capacity of 0.25 in. solid spheres was about 70, and that of 0.25 in. solid cylinders, 54. There is no doubt from the writers' experience that the capacity of solid spheres or beads is much lower than that of hollow cylinders of approximately the same diameter. If the above estimate is combined with the present value for Lessing rings, a capacity of not more than 48 cm. per sec. would be obtained for spheres of the same diameter.

Efficiencies much higher than those of chain packings have been found for certain special packings. For instance, Fenske, Quiggle, and Tongberg (1, 2) have determined the efficiencies of a number of unusual types of packing, including one very efficient packing consisting of one-turn wire helices  $\frac{1}{8}$  in. in diameter. Such a packing gave H.E.T.P. values roughly one-half those obtained with No. 18 chain.

When a glass packing must be employed the choice is rather limited. The efficiency of glass beads is good, but the capacity is low. Glass tubing about 7 mm. or less in diameter, cut into lengths approximately equal to the

diameter, will give good efficiency and capacity, provided that the walls of the tubing are quite thin. It is evident that thick walls would give a smaller free volume and a lower capacity, approaching the properties of beads. Wilson, Parker and Laughlin (9) describe a method for producing glass helices similar to the wire helices of Fenske, Quiggle and Tongberg (1, 2) mentioned above. Roper, Wright, Ruhoff and Smith (7) give additional information regarding the fabrication of these helices.

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# THE VISCOSITY OF VINYL ACETATE<sup>1</sup>

D. O. WHITE<sup>2</sup> AND A. C. CUTHBERTSON<sup>3</sup>

## Abstract

The viscosity of monomeric vinyl acetate has been measured over a range of temperatures from 0° to 60° C. Two equations were obtained which represent the results. The empirical equation is  $\eta = \frac{1.521}{(90 + t)^{1.25}}$ , and a theoretical equation is given as  $\eta(v)^{1/2} = 470 \times 10^{-4} e^{\frac{703}{T}}$ . The characteristic frequency has been obtained from the relation  $Nh\nu = \frac{RT}{\frac{1}{\mu} - 1}$ , where  $\mu$  is the ratio between the latent heat of evaporation and the heat of cohesion.  $\nu$  was found to be  $2.17 \times 10^{12}$ .

## Experimental

The measurements were made with a Pyrex viscosimeter of the Washburn and Williams (14) type. It had the following approximate dimensions—radius of capillary, 0.025 cm.; length of capillary, 19.5 cm. The volume of the upper bulb was 9.97 cc. A 50 cc. pipette was used for filling the viscosimeter. A thermometer, reading to 0.1° C., was calibrated in purified boiling benzene, acetone, and water, and in crushed ice, and all necessary corrections for barometric pressure and exposed stem were made.

The temperature of the water bath, which had a glass front, was controlled by means of a toluene regulator, and the bath was thoroughly stirred. The viscosimeter was so supported in the bath that when removed it could be replaced in a vertical position. On the average, the temperature could be controlled to within 0.002–0.003° C. The viscosimeter was always filled by means of the same 50 cc. pipette. The time of flow was measured by a stop clock which was wound up tightly prior to the measurement of the time interval. It was frequently compared with a master electric clock, and no error beyond the personal error could be detected. The viscosimeter was, before each experiment, carefully cleaned with a cleaning solution, washed with distilled water and dried by means of a current of filtered air.

### Calibration of the Viscosimeter

Benzene, carbon tetrachloride, water, and acetone were used in calibrating the viscosimeter. Benzene was first shaken with successive portions of concentrated sulphuric acid, washed with distilled water and shaken with mercury. The mixture was filtered, dried over calcium chloride and sodium, distilled and twice fractionally crystallized.

A sample of Merck's reagent carbon tetrachloride was used without further purification.

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Water was purified by distilling distilled water from an acid (sulphuric) permanganate solution, and then from an alkaline permanganate solution. It was kept in a flask, the inside of which was coated with paraffin.

Acetone was purified by the method of Shipsey and Werner (12), *i.e.*, sodium iodide was dissolved in hot acetone and allowed to crystallize at  $-8^{\circ}\text{C}$ . The mother liquor was poured off and the crystals of  $\text{NaI} \cdot \text{C}_3\text{H}_8\text{O}$  were dried by suction. The acetone was gently distilled off and dried for several days over phosphorus pentoxide.

Table I gives the results of the calibration of the viscosimeter.

TABLE I  
CALIBRATION OF THE VISCOSIMETER

Liquid	Temp., °C.	$\eta \times 10^6$	$K \times 10^{-7}$	% Deviation from mean
Benzene	6.88	8007 (7)	204.2	0.30
		7972 (8)	203.3	-0.15
	20.00	6490 (7)	204.3	0.35
		6475 (8)	203.8	0.10
	39.99	4913 (7)	202.7	-0.45
		4923 (8)	203.1	-0.25
Water	5.51	14850 (7)	202.5	-0.55
		14953 (8)	203.9	0.15
	20.00	10005 (7)	203.8	0.10
		10087 (8)	205.4	0.90
		10050 (3)	204.7	0.55
	40.00	6525 (7)	203.2	-0.20
6536 (8)		203.5	-0.05	
6560 (3)		204.2	0.30	
Carbon tetrachloride	22.28	9388 (8)	203.4	-0.05
Acetone	20.00	3225 (7)	201.9	-0.85
		3250 (4)	203.5	-0.05
		Mean	203.6	±0.30

NOTE:—The reference numbers in Column 3 refer to the source of the data. The values preceding reference No. 7 are from Thorpe and Roger, as given by Hatschek.

In obtaining some of the results another viscosimeter was used. It was calibrated at five temperatures with benzene. The value of  $K$  was  $(201.3 \pm 0.1) \times 10^{-7}$ .

#### Purification of Vinyl Acetate

The vinyl acetate\* used in these measurements contained a small amount of copper acetate, as a polymerization inhibitor, and traces of acetaldehyde and acetic acid. It was purified by two methods:— (i) by simple distillation

\* Supplied by Shawinigan Chemicals Limited.

through a long spiral column and collection of the middle portion of the distillate, which was dried over calcium chloride and filtered; (ii) by treatment with dilute 0.1 N sodium hydroxide solution, washing with water, drying with calcium chloride and redistilling. No difference was found in the viscosity of the samples within the limits of experimental error.

Andrade (1, 2) has investigated the variation of viscosity with temperature and has arrived at the following relation,  $\eta v^{1/2} = Ae^{\frac{c}{T}}$ , where  $\eta$  is the viscosity;  $v$ , the specific volume at temperature  $T$ ;  $A$ , a constant involving frequency of vibration, molecular dimensions and distribution of molecular field energy;  $c$ , a constant, proportional to about 1/10 of the total internal energy as derived from Van der Waal's equation.  $A$  was found to be  $470 \times 10^{-6}$  and  $c = 702$ , for vinyl acetate. The values for  $v$  were obtained from the data of Morrison and Shaw (11); and Green, Marsden and Cuthbertson (6).

The values for the viscosity of vinyl acetate at temperatures between 0 and 60° C. are given in Table II and shown graphically in Figs. 1 and 2.

TABLE II  
VISCOSITY VALUES—(a) EXPERIMENTAL; (b) THEORETICAL

Temp., °C.	(a) Viscosity, poises	Fluidity	(b) Viscosity, poises*	% error 100 ( $\eta_{\text{obs.}} - \eta_{\text{calc.}}$ ) $\eta_{\text{obs.}}$
0.10	0.005472	182.8	0.005432	0.7
2.70	0.005278	189.5	0.005256	0.4
4.82	0.005122	195.3	0.005117	0.1
8.42	0.004891	204.5	0.004896	-0.1
**11.23	0.004723	211.8	0.004732	-0.2
11.60	0.004707	212.5	0.004714	-0.1
13.33	0.004616	216.7	0.004616	0.0
**15.15	0.004509	221.9	0.004518	-0.2
†17.30	0.004404	227.1	0.004408	-0.1
19.40	0.004305	232.4	0.004303	0.0
**19.98	0.004269	234.5	0.004276	-0.2
21.10	0.004221	237.0	0.004222	0.0
†21.60	0.004200	238.2	0.004202	0.0
28.40	0.003900	256.7	0.003898	0.0
34.00	0.003688	271.3	0.003676	0.3
35.80	0.003612	277.1	0.003608	0.1
†40.70	0.003449	289.7	0.003435	0.4
49.87	0.003166	316.1	0.003144	0.7
††60.00	0.002922	342.5	0.002867	2.0

\* Values obtained from the formula  $\eta v^{1/2} = Ae^{\frac{c}{T}}$ , where  $A = 470 \times 10^{-6}$  and  $c = 702$ .

\*\* Washed with water and dried over calcium chloride.

† Purified by treatment with sodium hydroxide.

†† This sample probably polymerized slightly.

Those that are not marked were purified by simple distillation.

The viscosities calculated from the formula and the percentage errors calculated from  $100 \frac{(\eta_{\text{obs.}} - \eta_{\text{calc.}})}{\eta_{\text{obs.}}}$  are included in Table II, Columns 4 and 5.

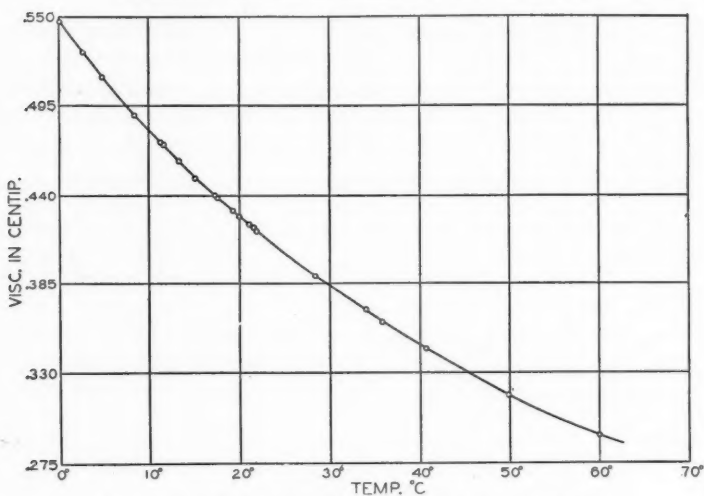


FIG. 1. Viscosity in centipoises plotted against temperature.

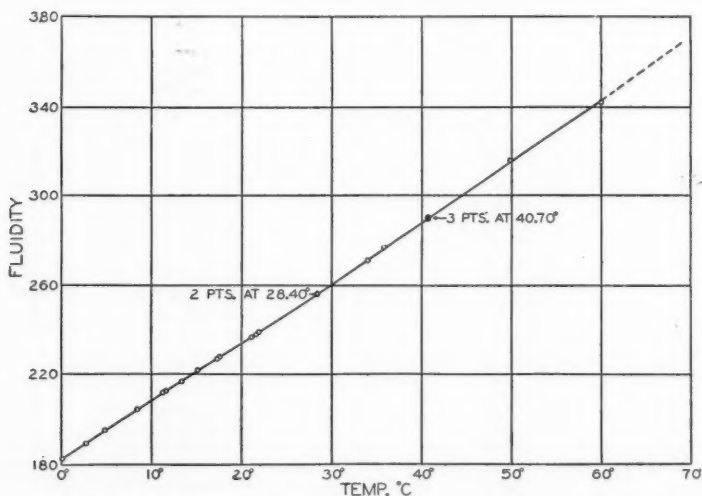


FIG. 2. Curve showing approximate proportionality between fluidity and temperature.

For convenience, an empirical formula has also been derived of the form  $\eta = \frac{1.521}{(90 + t)^{1.25}}$ , where  $t$  is the temperature in  $^{\circ}\text{C}$ . The equation represents the experimental data to an accuracy of 0.2%.

Drucker (5) has pointed out the relation  $\log 1/\eta = \rho + \mu \log p$ , where  $1/\eta$  = fluidity,  $\mu$  = ratio of the heat of vaporization and cohesion, and

$p$  = vapor pressure in mm. of mercury (9, 10). On plotting  $\log 1/\eta$  against  $\log p$ , a straight line is obtained whose slope is  $\mu = 0.231$ . The characteristic frequency,  $\nu$ , is given by  $Nh\nu\left(\frac{1}{\mu} - 1\right) = RT$ , where  $N$ ,  $h$  and  $R$  have their usual significance and  $T = 345.5^\circ \text{A.}$  ( $6, 9, 11$ ).  $\nu = 2.17 \times 10^{12}$ .

The results from which  $\mu$  may be obtained are given in Table III.

TABLE III

Temp., °C.	Log $1/\eta$	Log $p$ , mm.	Temp., °C.	Log $1/\eta$	Log $p$ , mm.
2.70	2.277	1.560	35.80	2.442	2.267
11.23	2.326	1.764	40.70	2.463	2.358
15.15	2.346	1.850	49.87	2.499	2.521
19.98	2.370	1.952	60.00	2.534	2.690
28.40	2.409	2.125			

### Discussion

An attempt has been made to obtain a representative calibration constant  $K$  for the viscosimeter, by using four liquids and averaging the viscosity values given by different observers for the same temperature. From the results presented it appears that benzene may be used with some degree of certainty.

It has been anticipated that the viscosity of vinyl acetate might have been affected by the method of purification (13, p. 49), which exerts a profound influence on the rate of polymerization. Such however does not seem to be the case.

Staudinger (13, p. 49) gives as the viscosity of monomeric vinyl acetate at  $20^\circ \text{C.}$  the value 0.00421 as compared with 0.00427 obtained by the writers and a value of 0.00432 given by Morrison and Shaw (11). For purposes of purification the vinyl acetate was steam distilled and shaken with sodium hydroxide solution. It was found by the writers that unless very dilute sodium hydroxide solutions were used, resins were formed owing to the fact that the vinyl alcohol is rapidly changed to acetaldehyde and gives aldehyde resins.

Andrade's relation between viscosity and temperature has been found very satisfactory. The interesting aspect of the equation is that the problem is approached from the point of view of the solid state of aggregation.

A linear relation between the logarithms of the vapor pressure and fluidity as pointed out by Drucker seems justified.

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# SORPTION OF WATER AND ALCOHOL VAPORS BY CELLULOSE<sup>1</sup>

BY J. K. RUSSELL,<sup>2</sup> O. MAASS<sup>3</sup> AND W. BOYD CAMPBELL<sup>4</sup>

## Abstract

Measurements were made of the amount of water vapor sorbed by beaten and unbeaten samples of kraft, unbleached sulphite and bleached sulphite wood pulps at relative vapor pressures ranging from 0 to 100%. Beating of the pulp made practically no difference to the degree of sorption at any relative vapor pressure. This indicated that beating caused no change in the hydration of the cellulose. Measurements were made of the sorption of methyl alcohol vapor by bleached sulphite, kraft and groundwood, and of the sorption of propyl alcohol vapor by bleached sulphite and cotton, all previously wetted with water and then dried. After sorption of alcohol, evacuation at room temperatures did not completely remove the alcohol. Measurements were also made of sorption of propyl alcohol by bleached sulphite and by cotton which had been dewatered by washing with propyl alcohol. The shape of the sorption curve was different for these samples, and the residual alcohol after evacuation was less. After a sample of cotton had been dried over phosphorus pentoxide in vacuo for a long period it was found to hold 0.35% of water by weight which could be removed by heating the cellulose to 100° C. This was regained from the pentoxide on cooling the cellulose.

The data are explained on the hypothesis that the crystalline submicroscopic elements of the cellulose structure are drawn together by internal tensile forces during the evaporation of the sorbed liquid, and that bonding between these elements may take place by the growing together of the crystal elements, leaving the structure internally stressed. On absorption, dissolution of these bondings takes place and the stresses are relieved as liquid enters the structure.

## Introduction and Summary

In the making of paper the main phenomenon is the adhesion which unites cellulose fibres when, having been thoroughly wetted with water, they are allowed to dry in contact with one another. The effect of water on cellulose is almost unique in that practically no other liquid is able to substitute for water in bringing about the important phenomena on which depend most of the uses of cellulose. It was the purpose of these studies to attempt to obtain a better understanding of the mechanism of the interaction of water and cellulose by comparing such interactions with corresponding interactions where cellulose and alcohols were involved.

Previous study of the water vapor pressure over beaten and unbeaten cellulose pulp showed that, within the limits of experimental error, there was no difference in the vapor pressures. This indicated that beating caused no change in the degree to which water was bound to cellulose. In the first part of the present work the same ground was covered in a manner essentially the same as before but with a more refined technique. The results show no reason for altering the earlier conclusion.

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The second portion of experimental work deals with the sorption of methyl alcohol vapor by papermaking pulps. The pulps used were groundwood, kraft and bleached sulphite, representative of uncooked wood, incompletely purified wood cellulose and highly purified wood cellulose. The amount of alcohol sorbed by the groundwood was greatest and by the bleached sulphite was least, but the general shape of the sorption curves was the same in all cases. The degree of sorption varied in each case according to the previous history of the sample. With the dried pulp there seemed to be some reluctance in regard to the taking up of alcohol until a moderate vapor pressure was reached, then the rate of sorption increased rapidly and followed a curve similar to that obtained in experiments with water vapor. On desorption to zero vapor pressure, the samples retained an appreciable amount of alcohol which was not removed by continued pumping. Curves of repeated adsorption showed a greater degree of pickup, and it was only after the third adsorption that the results were repeatable. In all cases a residue of alcohol remained in the samples at zero vapor pressure. The amount of alcohol sorbed was greater than the amount of water which similar samples sorb at the same relative vapor pressure when that pressure was low, but the reverse was the case at higher relative vapor pressures. The degree of hysteresis between adsorption and desorption was greater for alcohol than for water.

It is questionable what comparisons should be made to deduce the mechanism involved in these sorptions. If sorption is a matter of a layer of the liquid or highly condensed vapor adhering to all available surfaces, the basis of comparison should be volume sorbed against relative vapor pressure. If it is a matter of filling capillary passages, then the basis of comparison should be volume sorbed against capillary radius calculated from the lowered vapor pressure. But if, as will appear, sorption is a matter of release of strains controlled by internal liquid tension, then comparison should be made on the basis of volume sorbed against internal liquid tension calculated from the lowering of the vapor pressure. Comparison of the sorption of water and of alcohol on bleached sulphite pulp was made in each of these ways. Only the last comparison appeared to be of value. It indicated that the controlling factor in desorption was the drawing together of the fibre structure (shrinkage) under the influence of the internal liquid tension, and that the reverse action, modified by the effects of bonding, was effective on adsorption. According to this conception the residual alcohol is explained as being due to the limitation imposed by the obtainable internal tension, which is much lower with alcohol than with water.

The series of similar determinations with vapor of *n*-propyl alcohol was made chiefly for confirmation of this conception, in case it might be based on chance coincidence of the two sets of curves. The cellulose samples used were (i) bleached sulphite pulp as in the previous series, and (ii) a sample of cotton purified by boiling in dilute (1%) caustic soda solution. Two series of determinations were made with each of these materials. In the first, the cellulose samples were washed well with distilled water and were dried in

the apparatus before any alcohol was admitted. These will be designated "water washed". In the second series, the samples were washed with distilled water, and the water was removed as completely as possible by repeated washing with the alcohol. The samples were put into the apparatus while still containing liquid alcohol. These will be designated "alcohol washed".

The water washed samples behaved qualitatively in the same manner as did the samples similarly prepared in methyl alcohol. Quantitatively the sorption of *n*-propyl alcohol differed from the sorption of methyl alcohol much as the latter did from that of water. The reluctance to sorb the first portion of alcohol was more marked, the amount retained at zero pressure was greater, and the amount sorbed was greater at low vapor pressure and less at high vapor pressure. When the results were plotted on the basis of volume sorbed against internal tension, the points lay close enough to the equivalent data for methyl alcohol and for water to support the hypothesis that the internal tension modified by bonding was the governing factor in this sorption.

The alcohol washed samples were used because it was hoped that by removing the water in this way it would be possible to avoid or at least minimize the formation of the bonds which form on normal drying from water.

The phenomena of sorption of water and of alcohols on cellulose as shown by this work may be pictured as follows. The cellulose fibres in the plant constitute a structure which, though firmly united at various points, is yet rather open. In the plant, the spaces between the solid elements is filled with water and the structure is without strain. On removal of this water by evaporation the solid elements are drawn closer together by the internal tensile forces in the liquid, the deformation producing strains and corresponding stresses in the solid structure. Where the solid elements are drawn together sufficiently close, bonding may take place by crystallization so that these elements are united in the strained position, thus keeping the structure deformed after removal of the water. If water is allowed to return to the structure the reverse occurs, bonds are loosened and the structure may approach the original, unstrained condition, to a degree determined by the amount of adsorbed water. But, because of the bonding, the amount of water picked up by adsorption at any definite vapor pressure will be less than that held at the same vapor pressure during desorption. As far as the bonding conception is concerned this is the same as that advanced by Urquhart (11), though in the present work it is expressed somewhat differently because of the concept of the action of the internal tensile forces of the liquid. In the case of alcohols the action is modified by the lower solubility of the carbohydrate units, so that the number of bonds formed or loosened is much less. Two conditions may exist. (i) If the fibre is first wetted with water and then dried, many of the bonds formed during this drying are not loosened by sorption of alcohol. (ii) If water is displaced by alcohol without drying, few bonds are formed. Moreover, the maximum degree of internal tension which alcohol can exert is much less than that

produced by water, with the consequence that zero vapor pressure is reached with considerable alcohol still held, much more than is the case with water. There is also a possibility that pockets may be formed in the structure during drying and that liquid may be trapped in these pockets.

#### *Effect of Beating on Sorption of Water*

The action of the papermaker's beater has never been explained to general satisfaction. Mechanically it is simple, the action being the bruising of the fibres when well wetted with water. But the drastic changes produced by this action have led to suppositions of some far reaching change in the fibre. On continued beating the paper stock becomes glutinous to the feel when wet and, when dried, it forms a hard, dense mass quite unlike that formed from unbeaten stock. The wet, beaten stock is jelly-like and like other gels, shrinks and hardens on drying. For this reason there is a widely held opinion that some process of hydration takes place in the beater. In fact, the term hydration is generally applied to the process.

It was to test the existence of such change of degree of hydration that the present experiments were undertaken. They were based on the argument that if beaten cellulose pulp is more highly hydrated than the same pulp when unbeaten, it should hold more water at the same vapor pressure. Hence, when the water held is the same in amount, the more highly hydrated pulp should show a lower vapor pressure. Experiments along similar lines by Campbell and Pidgeon (4, p. 74) have shown that there was no difference in this respect produced by beating, and hence that beating caused no change in hydration. The present experiments were intended to verify this finding under more exact conditions.

#### *Apparatus*

#### **Experimental**

The apparatus employed was that shown in Fig. 1. For description this may be divided into two parts, that used to determine the amount of water held by the pulp sample, and that used to control the vapor pressure with which the sample was in equilibrium.

To determine the amount of water held by the sample it was suspended on a quartz spiral, *A*, the extension of which could be measured by a cathetometer. Since the extensions of the spirals used were found to be directly proportional to the weights suspended, the amount of extension was at all times a measure of the total weight, and when compared with the extension produced by the dry sample, a measure of the proportion of water held by the sample was obtained. The spiral was supported in a light glass frame, *B*, which had at the bottom a ring, *C*, through which passed the straight quartz fibre to which the sample was attached. On this straight fibre was a small crosspiece, *D*, which, by engaging with the ring prevented undue extension of the spiral. This device permitted attaching to the spiral samples carrying several times their weight of water, without impairment to the accuracy of the readings. As soon as the total load fell to that which could be safely

carried by the spiral, the crosspiece lifted clear of the ring and readings could be taken. It was essential that the wet sample should not touch the glass tube, since capillary forces would cause it to adhere. The frame and spiral were in turn suspended in a glass tube of which the lower half, containing the sample, was immersed in a constant temperature water bath.

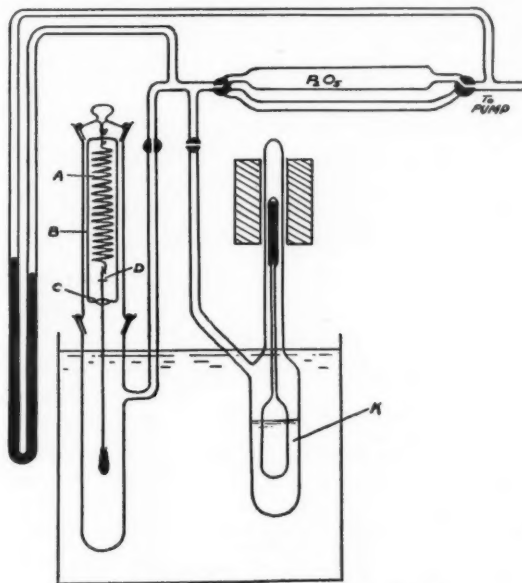


FIG. 1. Apparatus for water sorption.

For controlling the vapor pressure, the tube containing the sample was connected to a second tube, *K*, which contained sulphuric acid of strength appropriate to the pressure desired. The lower portion of this acid tube was also immersed in the same constant temperature water bath as the sample. During a test the acid was continually stirred by a glass float which was moved up and down by a solenoid outside the tube; the current in the solenoid was made and broken periodically through a switch operated by a windshield wiper. Between the acid tube and the tube containing the sample was placed a plug of glass wool to intercept any chance spray of acid. From the tube connecting the two, a side connection led directly or by way of a drying tube of phosphorus pentoxide to the vacuum pump. This side line was also connected to a mercury manometer, by means of which the vapor pressure in the system could be accurately determined.

In operation, the method was to attach to the spiral a sample of pulp containing a large excess of water, but which was of such a weight that the spiral would lift the bar from its supporting ring when the water content was reduced to about 40% of the dry weight of the pulp. The cell was opened

to vacuum for a few moments, after which the stopcock leading to the pump was closed. After waiting some time to allow any air dissolved in the water of the sample to escape, the vacuum was again applied to remove this air. This process was repeated several times—until the McLeod gauge showed that the amount of residual air was negligible. Air was removed separately from the acid solution in the same manner. When both sample and acid were sufficiently free from air, the two compartments were connected by opening the stopcock, and the sample was allowed to come to equilibrium with the atmosphere conditioned by the acid.

The fibre materials used in this study were bleached sulphite, unbleached sulphite and kraft pulps, all of good commercial grades. Beating was done in the laboratory beater. The extent of the beating is shown by the decrease in the freeness test given in each table. The laboratory beater causes less cutting in proportion to "hydration" than does a large size mill beater.

Results are shown in Tables I, II and III. From these it will be seen that beating produced practically no change in the degree of hydration as measured in this way. The beaten pulps showed a slightly greater amount

TABLE I  
SORPTION OF WATER VAPOR BY BLEACHED SULPHITE  
AT 27° C.

Rel. vap. pressure	Sorption, per cent of dry weight		
	Beaten (a)	Unbeaten (b)	(a)/(b)
<i>1st Desorption (from saturation)</i>			
0.689	11.8	11.7	1.01
0.417	7.3	7.0	1.04
<i>1st Adsorption (from 0 R.v.p.)</i>			
0.420	5.9	6.0	0.98
0.695	9.3	9.8	0.95
<i>2nd Desorption (from 0.695 R.v.p.)</i>			
0.425	6.5	6.3	1.03
<i>2nd Adsorption (from 0 R.v.p.)</i>			
0.426	5.9	5.9	1.00
0.690	9.5	9.3	1.02
0.900 (app.)	15.0	15.1	—
<i>3rd Desorption (from about 0.90 R.v.p.)</i>			
0.688	10.6	11.0	0.96
0.420	7.0	7.3	0.96
Average ratio			0.99

(a) Freeness (Can. Stand.), 65 cc.

(b) Freeness (Can. Stand.), 748 cc.

of water than the unbeaten. The formation of a slight amount of additional surface may be expected from the severe mechanical treatment, and this extra surface is consistent with the increased sorption shown in the data. On the other hand, equilibrium is reached much more slowly with the beaten pulps, and the difference, on the desorption cycle, is of the same order of magnitude as the experimental error. This explanation is hardly valid as the same difference appears on the adsorption cycle. The implications arising from this work are left for discussion later on in the paper.

#### SORPTION OF METHYL ALCOHOL

Determinations of the sorption of methyl alcohol were made without any anticipations of what the results

would indicate, but in the hope that the phenomena connected with this close homologue of water would throw some light on the relations with water. These hopes appear to have been realized.

The pulps used were commercial samples of ground-wood, kraft and bleached sulphite pulps. These received no preparation except thorough washing with distilled water to remove any water-soluble material. The samples were introduced into the cells while thoroughly wet. Dry weights were obtained by removing water by evacuation and absorption of vapor by phosphorus pentoxide. Only after being dried in this way were the samples exposed to alcohol vapor.

The control of alcohol vapor pressure by any method analogous to the use of acid solutions did not seem feasible. Therefore control was obtained by adding to or removing from the cells containing the samples small quantities of alcohol vapor. It was found by experience that stopcocks could not be relied upon when exposed to alcohol vapors for the weeks of exposure necessary. They were replaced by mercury seals in the vital part of the apparatus.

Fig. 2 is a diagram of the main features of the apparatus. The absorption

TABLE II  
SORPTION OF WATER VAPOR BY KRAFT PULP AT 20° C.

Rel. vap. pressure	Sorption, per cent of dry weight		
	Beaten (a)	Unbeaten (b)	(a)/(b)
<i>1st Desorption (from saturation)</i>			
0.960	34.0	31.6	1.07
0.701	13.8	13.3	1.04
0.623	11.8	11.8	1.00
0.412	8.3	8.0	1.04
0.272	6.6	6.2	1.06
0.177	4.9	4.7	1.04
<i>1st Adsorption (from 0 R.v.p.)</i>			
0.156	3.9	3.7	1.05
0.274	5.0	4.9	1.02
0.402	6.7	6.8	1.02
0.610	9.8	9.1	1.09
0.692	11.5	11.2	1.03
0.949	22.8	21.6	1.05
<i>2nd Desorption (from 0.949 R.v.p.)</i>			
0.690	13.2	12.4	1.06
0.630	11.5	11.0	1.05
0.440	8.4	8.1	1.04
0.256	6.2	6.0	1.03
0.150	4.7	4.5	1.04
<i>2nd Adsorption (from 0 R.v.p.)</i>			
0.148	4.1	3.9	1.05
0.260	5.3	5.1	1.04
0.400	7.0	6.4	1.09
0.610	9.6	8.9	1.08
0.690	11.3	10.3	1.10
0.942	22.4	21.7	1.03
Average ratio			
(a) Freeness (Can. Stand.), 80 cc.			
(b) Freeness (Can. Stand.), 720 cc.			

TABLE III  
SORPTION OF WATER VAPOR BY UNBLEACHED SULPHITE AT 20° C.

Rel. vap. pressure	Sorption, per cent of dry weight		
	Beaten (a)	Unbeaten (b)	(a)/(b)
<i>1st Desorption (from saturation)</i>			
0.947	33.6	31.3	1.07
0.836	20.2	19.5	1.03
0.690	13.0	12.8	1.02
0.609	—	11.1	—
0.398	7.2	7.2	1.00
0.252	5.7	5.6	1.02
0.150	4.2	—	—
<i>1st Adsorption (from 0 R.v.p.)</i>			
0.151	3.5	3.2	1.09
0.252	4.5	4.4	1.02
0.410	6.3	5.9	1.07
0.608	9.1	8.9	1.02
0.690	10.5	10.2	1.03
0.837	14.5	14.1	1.03
<i>2nd Desorption (from saturation)</i>			
0.947	30.8	29.0	1.06
0.845	20.4	20.4	1.00
0.692	13.1	12.9	1.02
Average ratio			
(a) Freeness (Can. Stand.), 54 cc.			
(b) Freeness (Can. Stand.), 670 cc.			

cell with its spiral balance and sample is shown at *A*. Three of these cells were connected to one header. The stock supply of purified alcohol was contained in the bulb *B*. The mercury traps for controlling the admittance

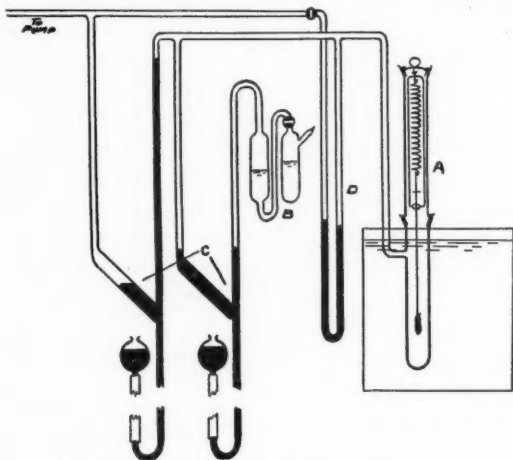


FIG. 2. Apparatus for alcohol sorption.

and removal of alcohol vapor are shown at *C*. The vapor pressure was measured by means of the mercury manometer, *D*, which was read with a cathetometer.

The alcohol was a good grade of synthetic methanol which was redistilled and dried with metallic calcium, then sealed into the apparatus and twice distilled in vacuum at room temperature. Only the middle portion was used. When finally distilled it was received into the bulb, *B*, which was then closed off.

The results of these determinations are set forth in Table IV and in Figs. 3, 4 and 5. It will be noticed at once that there is evidence of a reluctance for the dry samples of the sulphite and kraft pulps to take up the first portions of alcohol. This is not shown by the groundwood. The first adsorption curve was followed up to a relative vapor pressure of 52.5% of saturation, at which time the amount of alcohol sorbed by the three pulps was—bleached sulphite, 7.05, kraft 8.58 and groundwood 11.50%. At this stage the pressure was reduced to zero without intermediate readings in order to remove any residual air, which, according to some investigators, notably McGavack and Patrick (8), is responsible for hysteresis between adsorption and desorption. On reducing the pressure to zero it was found that appreciable quantities of alcohol were retained in spite of the fact that pumping was carried out with a good mercury vapor pump for seven days. The amounts so retained were 1.98% on bleached sulphite, 2.13% on kraft and 0.75% on groundwood. A second adsorption curve was carried right up to saturation as shown by the

TABLE IV  
SORPTION OF METHYL ALCOHOL AT 20.0° C.

Rel. vap. pressure	CH <sub>3</sub> OH sorbed, per cent of dry weight			Rel. vap. pressure	CH <sub>3</sub> OH sorbed, per cent of dry weight		
	Bleached sulphite	Kraft	Ground- wood		Bleached sulphite	Kraft	Ground wood
<i>1st Adsorption</i>				<i>3rd Adsorption—Concluded</i>			
0.000	0.00	0.00	0.00	0.2720	5.62	8.59	9.45
0.013	0.27	0.51	2.47	0.3970	6.83	9.69	11.10
0.054	0.61	1.54	3.98	0.5080	7.88	11.15	12.80
0.139	1.65	3.96	6.01	0.6090	8.76	12.20	13.80
0.197	2.59	5.00	6.77	0.7240	10.60	14.50	16.50
0.256	4.24	5.80	7.52	0.8220	12.10	16.10	18.20
0.401	5.84	7.26	9.55	0.8740	13.40	18.00	20.20
0.525	7.05	8.58	11.50	0.9180	14.80	19.70	21.80
<i>1st Desorption</i>				0.9560	16.90	22.20	24.20
0.000	1.98	2.13	0.75	1.0000	19.30	24.50	27.50
<i>2nd Adsorption</i>				<i>3rd Desorption</i>			
0.081	3.03	4.40	4.62	0.921	17.10	22.70	24.60
0.226	4.68	6.30	7.42	0.843	15.60	20.60	22.40
0.396	5.94	7.63	9.45	0.696	13.30	17.50	20.40
0.516	6.83	8.66	10.75	0.572	11.20	15.30	17.50
0.642	8.15	10.10	12.68	0.449	9.75	13.50	15.90
0.740	9.62	11.70	14.40	0.363	8.65	12.00	14.50
0.826	10.80	13.30	16.10	0.269	7.38	10.30	12.50
0.888	13.20	16.50	18.90	0.178	6.27	9.32	11.30
0.961	16.60	21.20	23.20	0.145	5.67	8.36	10.20
1.000	22.90	27.00	32.60	0.087	4.73	7.20	8.38
<i>2nd Desorption</i>				0.064	4.14	6.60	7.73
0.961	19.20	24.90	25.50	0.046	3.69	5.95	6.97
0.841	16.20	20.70	22.60	0.030	3.36	5.50	6.23
0.730	13.90	17.50	19.50	0.008	2.64	4.03	4.30
0.591	11.80	15.00	17.10	0.000	1.93	2.35	1.61
0.481	10.20	13.00	15.20	<i>4th Adsorption</i>			
0.385	8.92	11.20	13.40	0.032	2.42	3.60	4.62
0.296	7.92	10.10	12.00	0.144	4.40	6.45	7.41
0.227	6.77	8.66	10.60	0.296	6.11	8.15	9.67
0.148	5.56	7.34	8.81	0.446	7.32	9.61	11.1
0.085	4.51	6.16	7.41	0.571	8.59	11.30	13.4
0.000	2.08	2.12	0.75	0.723	10.60	13.90	15.8
<i>3rd Adsorption</i>				<i>4th Desorption</i>			
0.0105	2.15	3.52	4.08	0.6160	10.10	13.10	15.40
0.0277	2.48	4.55	5.27	0.5040	9.30	12.00	14.50
0.0673	3.30	5.50	6.23	0.3670	8.09	10.50	12.90
0.1100	3.85	6.16	6.87	0.2350	6.88	9.03	11.50
0.1850	4.46	7.19	7.63	0.1710	5.94	7.86	9.78
				0.0985	5.01	6.75	8.60
				0.0714	4.30	5.94	7.20

appearance of condensed alcohol. In the case of groundwood the first part of this curve was not distinguishable from the previous curve. In the case of the bleached sulphite and the kraft the second adsorption curve joined the first at about the point where the first had been discontinued.

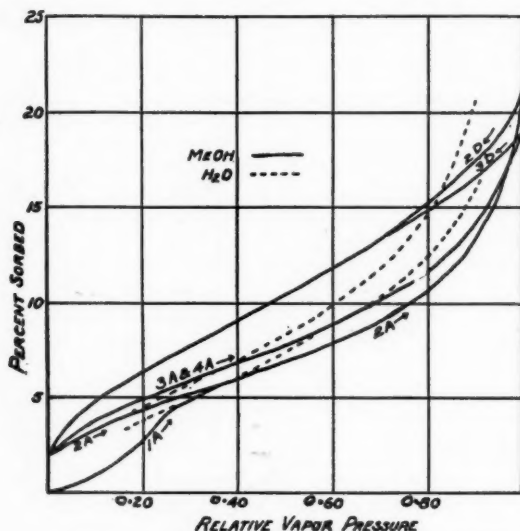


FIG. 3. Sorption of methyl alcohol by bleached sulphite.

A second desorption curve was determined from saturation down to zero pressure. Hysteresis between adsorption and desorption was very evident, and the amount retained at zero pressure was practically identical with that found after the first desorption.

A third adsorption was carried out to saturation and back to zero pressure. The adsorption curve ran above the previous one in all cases. The desorption curve was higher for the groundwood and the kraft, but was identical in the case of the bleached sulphite, except for a short

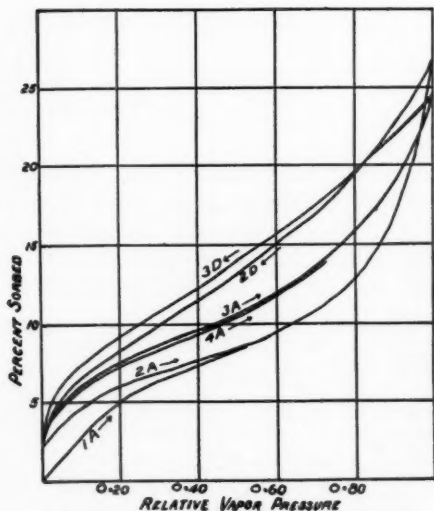


FIG. 4. Sorption of methyl alcohol by kraft pulp.

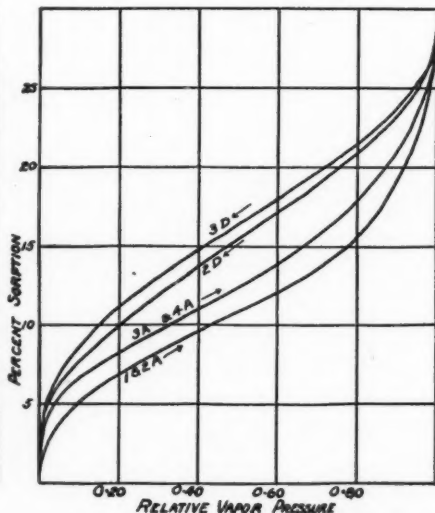


FIG. 5. Sorption of methyl alcohol by groundwood pulp.

portion near saturation where the difference in the amount of alcohol condensed on the sample evidently had an influence. The amount of residual alcohol at zero pressure was nearly the same as before in the case of the bleached sulphite, slightly higher for the kraft and nearly 1% higher for the groundwood.

A fourth adsorption was carried to 72% relative vapor pressure, over which range it followed practically the same course as the third adsorption. The desorption curve from this point gradually approached and finally joined the previous ones.

Further comment on these results will be found in the discussion.

#### SORPTION OF PROPYL ALCOHOL

After a study of the results of the sorption of methyl alcohol, it was decided to confine the experiments with propyl alcohol to the purer forms of cellulose. The samples used were bleached sulphite and cotton. The bleached sulphite was not treated in any way beyond a thorough washing in distilled water. The cotton was purified by repeated boiling in 1.0% caustic soda solution, followed by washing with distilled water (repeated seven times), then with dilute acetic acid and again with distilled water. Sorption by these materials was studied with the samples in two different original conditions. One set was put into the apparatus, wetted with water and this water was then removed by evaporation. In the case of the other set, substantially all the water was removed by long washing with alcohol without intermediate drying. The samples were put in the apparatus while still wet with the alcohol.

The alcohol used was supplied as being chemically pure *n*-propyl alcohol, but was further purified by drying with metallic calcium and twice distilling under vacuum, the final distillation being that into the storage bulb of the apparatus. This treatment should suffice to remove water and the most volatile impurities from the sample, but it would not remove other alcohols such as isopropyl. The alcohol used probably did contain some isopropyl alcohol, as shown by the fact that the vapor pressure was 17.08 mm. at 20° C. as against 14.5 mm. as given by the International Critical Tables for *n*-propyl alcohol. Over a temperature range of 10 to 30° C. the vapor pressure curve of the writers' material showed a regular displacement from that given by the data in the tables. In the calculation of relative vapor pressures the writers' value of the saturated vapor pressure was used.

#### *Sorption Measurements*

In making sorption measurements the apparatus and the general technique were the same as in the case of methyl alcohol sorption. In both cases the apparatus was completely sealed and free from stopcocks. The McBain-Bakr quartz spiral balance was used to determine the amount of alcohol sorbed. In some preliminary runs considerable trouble was encountered at very low pressures because of the tendency for mercury to distil from the manometer and seals to the samples. In the determinations reported, this difficulty was minimized but not entirely avoided by making the determinations at a

temperature above room temperature and by the interposition of a trap containing gold leaf. In spite of this precaution there was a certain gain in weight by the samples when the system was under vacuum. This increase could be due only to condensation of mercury on the samples. On this account there is some uncertainty as to the true dry weights. However, this uncertainty is not serious.

In order that the cycle of operations may be understood, a brief account of the determinations will be given as well as the presentation of the results in tabular form.

#### *Water Washed Samples*

The water washed samples of bleached sulphite and of cotton were put into the apparatus with excess water on the samples. Air was removed by repeated short time exposures to vacuum so as to remove the air with as little removal of water as possible. Weight readings were started when the relative vapor pressure of the water was about 0.66, and were continued until dry weight was obtained. During this drying the samples were kept at 25° C., but final dry weight was obtained by application of high vacuum with the samples at 35° C. to prevent condensation of mercury.

When the samples were dry, the temperature was again set at 25° C., alcohol vapor was admitted in successive small amounts, and the samples were held in each of these atmospheres until there was no apparent change in weight. The increase in weight was very slight until the vapor pressure of alcohol was above 50% of saturation, after which it mounted with comparative rapidity. This part of the data is not entirely satisfactory, as the greatest increase in weight took place during two weeks when no observations were made. It is accordingly uncertain whether the earlier low values of sorption were really due to small take-up at equilibrium, or were due to a very slow approach to equilibrium values not really reached. In view of similar behavior (at a lower vapor pressure) with methyl alcohol, it is thought that these low values were real. This adsorption cycle was continued up to the point where the samples were in contact with saturated vapor and some liquid alcohol had condensed in the cells containing the samples.

Following this adsorption, desorption points were determined, at 25° C., by removing successive small portions of alcohol vapor and waiting until equilibrium was reached. This desorption was continued until there was no measurable vapor pressure, and the samples had been subjected to high vacuum (mercury diffusion pump) for 10 days. During the last six days of this experiment the temperature was raised to 30° C. but no change in weight occurred.

A second adsorption curve was then determined in the same manner as before, but at 20° C. This was followed by a second desorption, which, because of the temperature of the water supply, was run at 26° C.

The results of the determinations on these water washed samples are given in Table V and Figs. 6 and 7.

TABLE V  
SORPTION OF PROPYL ALCOHOL VAPOR BY WATER WASHED SULPHITE AND BY  
COTTON CELLULOSE

Rel. vap. pressure of alcohol	Per cent sorbed by		Rel. vap. pressure of alcohol	Per cent sorbed by	
	Sulphite	Cotton		Sulphite	Cotton
<i>1st Adsorption, at 25° C.</i>			<i>2nd Adsorption, at 20° C.</i>		
0.095	0.13	0.10	0.068	4.38	3.48
0.230	0.32	0.21	0.098	4.55	3.51
0.418	0.52	0.42	0.144	5.55	4.26
0.539	2.19	1.22	0.274	6.62	5.07
0.680	2.43	1.38	0.391	7.28	5.54
0.995	5.13	3.07	0.544	8.40	6.37
Saturation	11.9	8.3	0.675	9.10	6.63
			0.795	9.95	7.23
<i>1st Desorption, at 25° C.</i>			0.910	12.67	8.80
0.940	11.30	8.16	0.940	14.51	10.06
0.830	10.72	7.78	0.980	21.9	12.92
0.700	10.40	7.62	Saturation	35.7	20.6
0.565	10.02	7.37	<i>2nd Desorption, at 26° C.</i>		
0.472	9.85	7.26	0.932	21.10	14.79
0.424	9.57	7.05	0.788	12.45	8.97
0.348	9.08	6.84	0.688	12.06	8.81
0.276	8.50	6.45	0.532	11.35	8.42
0.254	8.15	6.04	0.424	10.99	8.16
0.230	7.91	5.88	0.348	10.15	7.59
0.184	7.74	5.75	0.280	9.64	7.25
0.161	7.47	5.54	0.208	8.85	6.63
0.151	6.93	5.18	0.132	7.85	5.90
0.115	6.70	4.97	0.088	7.15	5.51
0.080	6.20	4.63	0.068	6.46	4.97
0.0604	5.90	4.45	0.040	5.99	4.68
0.0425	5.14	3.90	0.036	5.56	4.37
0.0290	4.76	3.93	0.028	5.32	4.16
0.00	4.04	3.36	0	4.34	3.48

#### Alcohol Washed Samples

The alcohol washed samples were prepared as follows. Portions of the sulphite and cotton cellulose samples, prepared as described for water washed material, were taken, and, without drying, were diluted with alcohol. After several hours soaking, the larger portion of the now diluted alcohol was removed by gentle squeezing. Compensation was made for this loss by the addition of strong alcohol. The washing with alcohol was repeated many times, until the water content of the residual alcohol was estimated to be less than 2%. The samples, wet with an excess of this nearly pure alcohol, were then hung on the spirals and put in the cells.

Because of the uncertainty regarding the water content, the weights of the samples during the first evacuation, and the corresponding vapor pressures, are not recorded here. As the alcohol

used had at 20° C. a vapor pressure of 17.08 mm. as compared with 17.53 mm. for water, it was considered that the small water content of the residual alcohol would not seriously affect the amount retained. A difficulty was experienced in obtaining the final weights in vacuum. On subjecting the samples to vacuum, the weights quickly reached a minimum and then started to increase. This increase was due to condensation of mercury on the samples when the room temperature or the temperature of mercury in the traps, etc., was above that of the bath. The extra weight picked up during this drying period was deducted from the total weight increase in the subsequent adsorption, and the balance considered to be alcohol.

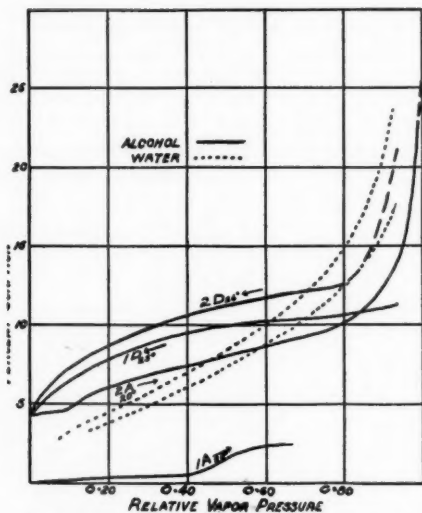


FIG. 6. Sorption of propyl alcohol by bleached sulphite (water washed).

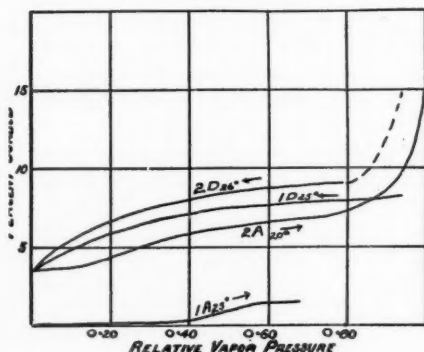


FIG. 7. Sorption of propyl alcohol by cotton cellulose (water washed).

One adsorption was carried to saturation at 20° C., followed by a desorption to vacuum dried weight, for which again the lowest weight reached was taken. There was a similar pickup of mercury at this stage of vacuum treatment for which allowance was made in subsequent treatment. This subsequent treatment consisted in repeated addition and evaporation of water vapor to remove residual alcohol not removed by vacuum. The loss of weight by this treatment was considered to be due to removal of alcohol.

### Mercury Condensation

During the work the question arose as to whether the mercury that was picked up by the samples when under high vacuum was deposited as the result of condensation of mercury vapor, or whether it was actually sorbed. The following experiment was carried out, and it indicates that the process was one of condensation.

A sample of cotton cellulose was hung on a quartz spiral in a cell such as that used in the main work. Between this and a mercury reservoir there was interposed a coil of tubing such that it could be surrounded by a water bath which was kept at a temperature of about 3° C. by a flow of tap water. The mercury was at room temperature (about 25° C.), while the sample was at 20° C. The whole system was kept evacuated by means of a mercury diffusion pump. Under these conditions there was no increase in the weight of the sample in 20 days.

On stopping the supply of cold water to the intermediate cooling coil, the weight of the sample promptly increased, and in 40 days the extension was too great to be read by means of the cathetometer, *i.e.*, the quantity condensed was more than 27% of sample weight. Then the cooling was resumed, and it was found that the weight of the sample returned almost exactly to its original value although the temperature of the cooling coil was now about 14° C., which was the tap water temperature at this time.

The correction for weight of condensed mercury in obtaining the dry weight of pulp used is not altogether satisfactory. The manner in which this correction was made is as follows:—The first drying under vacuum gave a low total extension of 100.10 mm. for the sulphite cellulose. This is considered to be the "dry weight" of the sample plus residual alcohol not removed by vacuum. After the second vacuum drying, the sample contained both residual alcohol and condensed mercury. Treatment with water vapor reduced the weight by an amount represented by 2.38 mm. extension which is taken as the amount of residual alcohol. The assumption is then made that this same amount of residual alcohol was present when the first "vacuum dried weight" (100.10 mm. extension) was determined. The "dry weight" of the sample is then the difference between these two, *i.e.*, 97.72 mm. Just prior to the starting of the first adsorption, the sample had picked up mercury corresponding to 2.34 mm. In the presence of a considerable pressure of alcohol vapor none of this would be lost during the adsorption, so this amount (2.34 mm.) is deducted from these observed extensions in order to obtain the extensions due to sample plus alcohol during this period. During desorption, however, some of the condensed mercury might be lost by entrainment with the alcohol vapor evaporating from this sample. The low extension reached on evaporation was 101.90 mm. Allowing 100.10 mm. as a measure of the weight of sample plus residual alcohol, the condensed mercury present at this time was 1.80 mm. and an allowance of this amount was made throughout the desorption data. The difference of 0.54 mm. is considered as mercury lost by evaporation. Similar corrections were made for the cotton sample.

Errors involved in this adjustment are included in the values for high sorption. During the adsorption period the amount of mercury is likely to increase. During the desorption period it probably decreases as desorption proceeds, so that the values for sorbed alcohol in this series may be

slightly high. In addition to this allowance for mercury there is, of course, a slight uncertainty as to whether all the alcohol was removed by water. Error from this source is probably inappreciable.

The alternative to this is to consider that all mercury picked up on first vacuum drying remained on the samples throughout the desorption. This would lower the assumed dry weight by 0.54 mm. extension and increase the amounts in the adsorption series. It would make practically no change in the desorption series since the extensions attributed to sorbed alcohol would be the same as before. Only the dry weight on which percentages are based would be changed by about 0.6%.

The results of the determinations on the alcohol washed samples are given in Table VI and Figs. 8 and 9.

TABLE VI

SORPTION OF PROPYL ALCOHOL VAPOR BY ALCOHOL WASHED SULPHITE AND COTTON CELLULOSE

Rel. vap. pressure of alcohol	Per cent alcohol sorbed by		Rel. vap. pressure of alcohol	Per cent alcohol sorbed by	
	Sulphite	Cotton		Sulphite	Cotton
<i>Adsorption at 20° C.</i>			<i>Desorption at 26° C.</i>		
Vacuum dried*	2.44	1.13	0.918	—	30.54
0.014	3.01	2.26	0.849	18.62	13.08
0.046	3.78	3.14	0.785	17.31	12.48
0.103	5.16	4.23	0.672	15.98	11.76
0.241	6.69	5.47	0.593	15.12	11.31
0.379	8.04	6.45	0.522	13.67	10.43
0.518	9.68	7.58	0.460	12.89	9.89
0.630	11.11	8.62	0.412	11.91	9.32
0.761	13.65	9.96	0.330	10.83	8.48
			0.279	10.19	8.03
0.890	22.18	18.10	0.214	9.10	7.15
0.916	28.50	23.68	0.174	8.49	6.63
Saturated	—	31.58	0.107	6.49	5.25
			0.067	5.63	4.48
			Vacuum dried†	2.44	1.13

\*Lowest weight. Mercury picked up before adsorption of alcohol, in per cent of weight of sample, on sulphite 2.40%, on cotton 1.92%.

†Lowest weight. Mercury on sample at this point, on sulphite 1.80%, on cotton 0.98%. Alcohol content taken as equal to weight lost on treating with water vapor.

#### *Effect of Temperature on Residual Alcohol*

The effect of temperature on the amount of residual alcohol held by cellulose was examined at temperatures between 2° and 40° C.

Samples of sulphite and cotton cellulose were placed on spirals and dried over phosphorus pentoxide in high vacuum to a constant weight. Methyl alcohol vapor was next admitted until condensation in the cells was noted. Samples were kept in this vapor for two days at 2° C., and the alcohol vapor was pumped off until the sample weight was constant for two days. (Conden-

sation of mercury vapor was prevented by means of a cooled trap between the samples and the mercury diffusion pump.) The samples at this point showed alcohol sorption of 1.83% by the cotton and 2.18% by the sulphite. Increase of temperature caused a regular drop in this amount, so that at 40° C. the amounts retained were 0.58% by the cotton and 0.97% by the sulphite. This statement that the drop is a regular or a straight line relation must be qualified slightly, because, at about room temperature, there was an interval of about 4° in which no change of weight was noted. This break in what are otherwise straight lines is believed to be due to an experimental error.

#### *Effect of Temperature on Residual Water*

The weight of the cellulose after it has been dried in vacuum over phosphorus pentoxide is usually taken as the dry weight. This is not an absolute value but is reproducible. The following experiment was made to determine the effect of temperature on the water retained in such "dry" cellulose.

A sample of cotton was hung on a spiral in a tube connected, by a side arm, to a bulb containing phosphorus pentoxide, and the whole thoroughly evacuated and sealed off from the pump. The extension of the spiral was then read. This gave the dry weight of the sample. This did not change over a period of several days. Then the lower end of the tube containing the sample was immersed in water at various temperatures, and the loss in weight determined at temperatures up to 100° C. (Table VII).

On lowering the temperature to that of the room the original dry weight was obtained. The experiment was repeated several times and can indicate

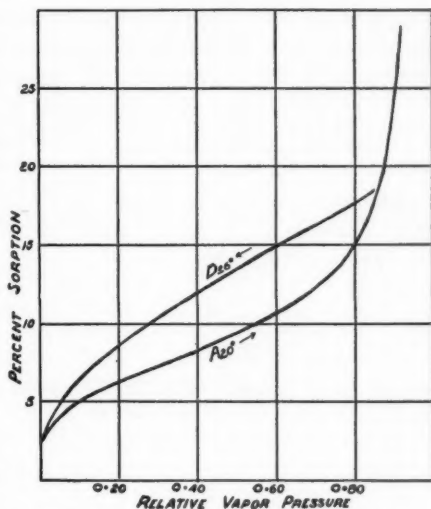


FIG. 8. Sorption of propyl alcohol by bleached sulphite (alcohol washed).

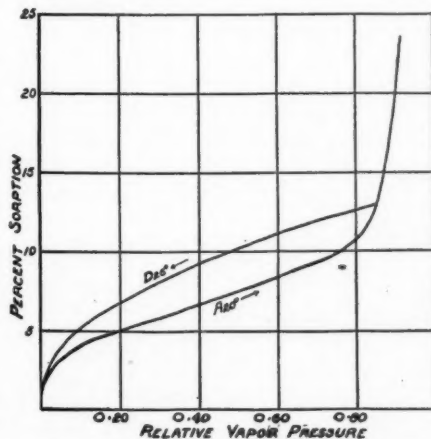


FIG. 9. Sorption of propyl alcohol by cotton cellulose (alcohol washed).

only that cellulose, when so dried, still retains water with a vapor pressure lower than that retained by phosphorus pentoxide.

TABLE VII  
LOSS IN WEIGHT (ACCURATE TO  
LESS THAN 0.04%)

Temp. °C.	%
40	0.04
60	0.10
80	0.17
100	0.35

condensed and the water froze in the capillary. The water was quickly adsorbed by the cellulose when allowed to thaw.

In another experiment this water was made apparent by using a large sample of cellulose in a bulb connected by a side arm to a capillary tube in which the vapor could be condensed by a carbon dioxide freezing mixture. The cellulose was dried by application of high vacuum and in the presence of phosphorus pentoxide for three weeks and then sealed off from the vacuum and drying bulb. On warming the bulb containing the cellulose and cooling the capillary in the freezing mixture, vapor condensed and the water froze in the capillary. The water was quickly adsorbed by the cellulose when allowed to thaw.

### Discussion

In discussing these results it is difficult to distinguish at all points between what is proved and what is speculative. In the authors' opinion the phenomena are associated with the action of physical forces of surface tension and internal liquid tension combined with effects due to surface solubility of cellulose in the liquids concerned, all acting on an open but well bonded solid structure of cellulose. Of the existence of these forces of surface tension and internal liquid tension there is no doubt. There is also little doubt that cellulose consists of a well bonded structure of small units among which water and other liquids may be held. The surface solubility of cellulose, particularly the peculiar character of this solubility, is a much more speculative conception.

As the possibilities of internal liquid tension have not been drawn upon to any great extent in general explanations, and as liquids are not usually regarded as having tensile strength, something may be said about this phenomenon. Consider a capillary tube in which a liquid has risen by capillary action to some height,  $h$  cm. If the pressure of the liquid at the general surface level is taken as zero, then the liquid in the tube, being at a higher level, must be under a negative pressure, *i.e.*, under tension. At points in the tube corresponding in elevation to the general liquid level, this tension is just balanced by the pressure due to the column of liquid above it. Consequently the tension at the top of the column is equal to the weight of the column. The tension may be calculated by either of two methods: (*a*) from the known surface tension of the liquid, together with the known diameter of the capillary tube; or, (*b*) from the reduction of the vapor pressure of the liquid at the top of the tube. Method (*a*) is merely the inverse of the usual method for determining surface tension from capillary rise. Method (*b*) depends on determining the tension at the top of a column of liquid of a height equal to the height of a column of vapor necessary to reach a definite

degree of pressure lowering. As this latter method requires no knowledge of the surface tension in extremely small capillaries or of the size of such capillaries, it is more generally applicable. The tension,  $P$ , may be calculated from the formula

$$P = \frac{195 T \sigma \log (p_0/p)}{M} \text{ kg. per sq. cm.,}$$

where,  $T$  is the absolute temperature,  $M$  is the molecular weight of the liquid when in the gaseous state,  $\sigma$  is the density of the liquid and  $p/p_0$  is the vapor pressure at the surface of the liquid in the capillary relative to the normal vapor pressure over a plane surface.

That cellulose has a structure of solid units bonded together in some way with open or potentially open spaces is evident from the X-ray observations by Katz (6), who concluded that, since cellulose swollen by water or salt solutions did not show any change of crystal structure, the water must be between the crystals and not in them. Botanical evidence also points to the same conclusion. The fibrillation or splitting of fibres evident as a result of paper mill beating is probably a manifestation of the same thing, though it may be, in part, a matter of crystal cleavage. That there is a considerable degree of bonding of the structure is evident from the fact that there is a well defined limit to the swelling in water. If there were no bonding to restrain it, the swelling would proceed to the point of complete dispersion of the units.

These two facts, a bonded but open network structure of solid cellulose units and the effects of the forces of surface and internal liquid tension, account for many of the phenomena of the sorption of vapors by cellulose, but do not so do completely. Something must be due, in addition, to the specific nature of the liquid concerned. In discussing the hysteresis between the adsorption and the desorption parts of the cycle of water sorption, Urquhart (10, 11, 12) points out that, in the plant, the cellulose is laid down in the presence of water and that much of this water is closely associated with the hydroxyl groups of the cellulose. On removal of the water, by drying, the affinities of the hydroxyl groups become satisfied with each other and so form bonds between parts of the structure which, before drying, were free. He considers that deformations brought about in this way are responsible for the internal stresses evident in dry cellulose.

According to our view the strains are brought about by the action of the liquid forces previously mentioned, but the dry material is held in the strained position by a bonding mechanism essentially the same as he postulates.

The work of Haworth (5), Stamm (9), and others leaves little doubt that the cellulose molecule is a long chain of 100 or more glucose anhydride units. Since glucose is quite soluble in water and short chains of similar character are also quite soluble in water, it seems reasonable to suppose that the insolubility of cellulose may be more apparent than real, in the sense that the units of the chain may be soluble though the chain itself is not. In a saturated solution of a substance such as sugar, having molecules of moderate

length, there is a continual process of solution and crystallization going on at the surface of any crystal of sugar in contact with the solution. The solution being saturated, the rates of these two processes are equal. In the case of cellulose, we conceive of the same being true with respect to the unit groups of the chain, but that the whole molecule can escape from the crystal only in the rare event of all its constituent units being simultaneously dissolved. Such a condition would permit of ready bonding by recrystallization even without very close contact, since individual cellulose molecules might become attached to more than one crystal. In liquids such as alcohols, which are not good solvents for sugars, the possibilities of forming such unions or of loosening any which have formed are much less. Such a condition may be described as one of "surface solution" or, if water is the solvent, as "surface hydration".

While the hypothesis of the mechanism of sorption by cellulose here advanced was evolved largely from these experiments, the discussion will be simpler if the hypothesis is presented first and the experimental findings then examined to see how they fit.

As Urquhart pointed out, cellulose is formed in the plant in the presence of excess water, and when first formed is without strain. In drying out, the water filling the spaces in the fibre, and even in the spaces between the fibres, exerts a tensile force drawing the whole together. Wherever this force is resisted by the rigidity of the structure, deformation of the structure necessarily results. The intensity of such force is surprisingly quite large. Two cylindrical fibres of 0.001 mm. diameter, in contact with each other, but with enough water to fill the "nip" between them, will be pulled together with a force of about one and a half atmospheres by surface tension alone. The intensity of the pressure over the very small area of actual contact will be many times this. If the structure is sufficiently rigid to withstand these stresses without its parts coming close enough to be bonded by recrystallization, then the water column will break leaving two independent cellulose surfaces. In general, this is what happens in a mass of fibres. A few bonds are probably formed between individual fibres when a mass of cotton dries from water, but such bonding is not extensive. However, if the diameters of the fibre units are reduced, as by the fibrillation mechanically brought about in beating, then the intensity of the tensile forces is greater and the rigidity of the fibre units is less, so that much more bonding results.

In an individual fibre there is a similar condition, intensified because the units are so much smaller. When loss of water proceeds so far that water begins to be evaporated from the exceedingly fine passages in the fibre wall, the internal liquid tension rises to high values. Even at 90% relative humidity it is equivalent to an external pressure of 142 atm. In rigid gels such as silica gel or charcoal the structure resists the deforming force for the most part and maintains its dimensions, but in non-rigid gels such force causes shrinkage in proportion to the volume of liquid lost by evaporation. Portions of the solid structure brought into contact by such deformations may become

bonded together by recrystallization if the liquid is one that can form such "surface solutions" as were earlier described. Such is the case with cellulose and water. In the case of rigid gels the liquid simply evaporates and leaves a corresponding volume of empty space. McGavack and Patrick (8) found that, in the case of silica gel, the volumes of all liquids sorbed were substantially the same, indicating that the capillary space available was the main factor in this case. Under such circumstances there should be no hysteresis between adsorption and desorption, and these investigators claim that no hysteresis is found when proper precautions are taken to avoid the presence of non-condensing gases. Their conclusions, even if valid for rigid gels, should not be extended to cover non-rigid gels such as cellulose.

When the alteration in properties of pulp brought about by the beating process is kept in mind, the data on water sorption of beaten and unbeaten pulps are seen to agree with these ideas. Since the only possible chemical reaction in the beater is one between cellulose and water, and, as this does not take place, as shown by the unaltered character of the vapor pressure curve, it follows that the changes effected by beating are purely physical. Moreover they must be physical on a scale involving units somewhat larger than those generally considered as colloidal and therefore within microscopic range. The fibrillation of the stock, as seen on microscopic examination, is of such a nature.

With the assumption that some form of bonding normally occurs when cellulose surfaces dry in actual contact with each other, the changed properties of paper stock brought about by beating are accounted for by such fibrillation, and the action of surface tension and internal liquid tension on the greatly increased external surface available for such bonding. This phase of the problem was discussed at length by Campbell (1, 2, 3) in earlier papers.

The sorption of alcohol vapors, according to the hypothesis outlined, will differ from that of water vapor chiefly because of (i) the difference in the degree to which bonding is affected, (ii) the much lower intensity of the surface tension, and (iii) lower internal tensile forces at similar relative vapor pressures.

As examples of different degrees of loosening of bonds uniting fibres in paper, the following tests may be cited. A sample of paper was tested under the usual paper testing conditions (70° F., 65% relative humidity) and also when wet with water, methyl alcohol, ethyl alcohol and propyl alcohol. The results are shown in Table VIII. (Tensile test.)

The destructive effect of water on the bonds formed between the fibres is evident, as is also the progressively smaller effect of wetting as higher alcohols are used.

Since the sorption phenomena with the alcohols seem to be of similar nature for the different cellulose samples, differing only in degree, it will suffice to consider only the bleached sulphite pulp since it was used with both methyl and propyl alcohols.

TABLE VIII

Wetting substance	Tension, kg.
Water	0.69
Methyl alcohol	2.32
Ethyl alcohol	4.63
Propyl alcohol	5.77
Dry	7.28

Considering first the water washed samples, *i.e.*, those that were first wetted with water and then dried, we note that on first adsorption there is a reluctance, on the part of the sample, to sorb alcohol until the vapor pressure rises considerably. This is much more marked with propyl than with methyl alcohol. In the case of the propyl alcohol, adsorption was only slight until the vapor was nearly saturated, and no exact values were obtained in this region. With methyl alcohol the sorption increased rapidly after the relative vapor pressure reached 0.20, and was nearly normal at a relative vapor pressure of 0.40. While there is some doubt as to whether these values represent true equilibria or only an exceedingly slow rate of pickup, they do accord with the general ideas of the relative loosening of bonds in the two liquids. It is to be expected that the bonds formed during the drying from water will be difficult to loosen in alcohol.

The first adsorption of methyl alcohol was carried to a relative vapor pressure of only 0.525, after which desorption to zero pressure was carried out without intermediate measurements. A second adsorption curve merged with the first about where the first was discontinued. This second adsorption was carried to saturation and a desorption curve from this point to zero pressure was obtained. A third adsorption curve to saturation was only slightly above the second, and a third desorption was identical with the second except for a short range near saturation, where values are probably influenced by the amount of liquid between fibres as well as by that in the cellulose structure itself. A fourth adsorption was identical with the third as far as it was carried (relative vapor pressure 0.723). From this point the desorption curve merged with the other two desorption curves at a relative vapor pressure of about 0.25.

If the third adsorption and desorption curves are taken as representing reproducible conditions, it is to be expected, according to our hypothesis, that, when volumes of sorbed liquid are plotted against internal liquid tension, the alcohol adsorption values should lie below the water adsorption values for the same reason that the water adsorption values lie below the desorption values, *viz.*, because fewer bonds are loosened. The data, plotted in this way in Fig. 10 show that this is the case.

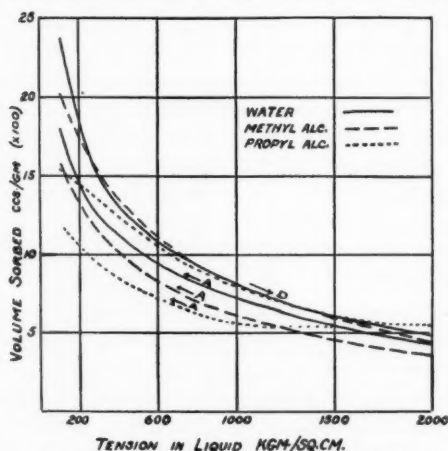


FIG. 10. Sorption (by bleached sulphite) plotted against liquid tension.

On desorption, however the bonds play a minor role, the main factor being the action of internal liquid tension drawing the structure together. The effect of bonding cannot be altogether

absent because, at saturation, alcohol does not cause a loosening of as many bonds as does water and consequently in this region a somewhat greater volume of water may be expected for the same internal stress. But over the greater part of the desorption curve the volumes of alcohol and of water should be the same for the same internal liquid tension. This is also found to be the case.

The propyl alcohol sorption cycles were not repeated as fully as were those of methyl alcohol. The first adsorption showed comparatively little pickup. A rather sudden rise at about a relative vapor pressure of 0.50 occurred when the apparatus was unattended for some time. This phenomenon may or may not be significant. However, not much alcohol was sorbed until the sample was wet with condensed liquid at saturation. After the first desorption curve was determined, a second adsorption was made which was quite different in character from the first. After a short initial lag, which was rather like that found in the first adsorption of methyl alcohol, the general form of the curve was similar to those previously found. A second desorption curve lay somewhat above the first. Unfortunately further work was impossible.

When the second adsorption curve for propyl alcohol was plotted as volume sorbed against internal liquid tension, it was found to be displaced from that of methyl alcohol in the same sense and to about the same degree as the latter curve was displaced from that of water. There is some uncertainty, however, about the lower end corresponding to the part where a lag in adsorption occurred. A possible explanation of this will be suggested later.

On desorption, by the same argument as advanced in the case of methyl alcohol, it is to be expected that internal liquid tension will be the governing factor. In accordance with this, the curves obtained by plotting volumes of water, methyl alcohol and propyl alcohol against internal tension are identical, within the range of experimental error.

The determinations with alcohol washed samples of cellulose were made to ascertain what would be the effect of eliminating the water formed bonds as far as possible. It was thought that the replacing of the water by alcohol without intermediate drying would leave the structure in much the same state of dispersion, with but a much diminished chance of forming new bonds as the liquid evaporated. The idea was much the same as that of Kistler (7), who replaced the water in several gels in this manner, and finally replaced the substitute liquid by air without allowing surface tension to come into play to compress the gel.

Since the bonding in the alcohol washed material is, presumably, less than that in the water washed, the structure should be less rigid and therefore more compressible. It should accordingly show a more rapid decrease of volume of sorbed liquid as the internal liquid tension is increased. Reference to Fig. 11 shows that this is the case.

On adsorption on the alcohol washed material, the release of bonds should approximate the release when water is absorbed by a water washed sample, because in each case the bonds are being loosened by the same liquid in which

they were formed. But in the alcohol washed sample the volume has been decreased in part by rearrangement of structure possible because of less rigid bonding. Hence, for the same volume of voids available for each liquid,

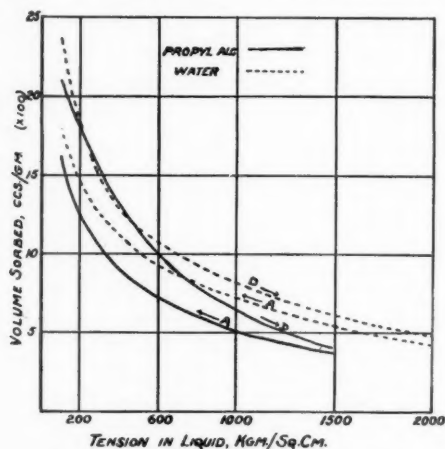


FIG. 11. Sorption (by bleached sulphite-alcohol washed) plotted against liquid tension.

there will be less stress in the cellulose structure tending to expansion. In consequence, at any value of the internal liquid tension there will be less volume of the liquid sorbed. Reference to Fig. 11 shows that this is also the case.

The fact that alcohol is retained by all samples at zero vapor pressure, or at least at a pressure as low as could be produced by a good mercury diffusion pump operating for a week, must be accounted for. It may be due to the fact that the limit of the maximum internal tension is the normal internal pressure of the liquid. Exact values for the internal pressures of the alcohols are lacking but approximations are generally of the order of 3500 kg. per sq. cm. Measurements above about 1500 kg. per sq. cm. or a relative vapor pressure of 0.012 are not available from this work in the case of propyl alcohol or above about 2000 kg. per sq. cm. or a relative vapor pressure of 0.035 in the case of methyl alcohol. At these pressures the desorption volumes of water washed samples agree for all three liquids. But from the volume of propyl alcohol retained after much evacuation it seems that, for propyl alcohol, the limit is about 1700 kg. per sq. cm. If this is the sole factor in this range, either the pump could not produce a better vacuum than about 0.16 mm., or the accepted approximate internal pressure values of the alcohols are high. It is more probable that some other factor is involved.

If the structure of the cellulose is such that these voids which contain the liquid may be closed off by bonding of a comparatively narrow neck, then it is conceivable that some parts might be sealed off while still containing liquid which would not be removed by evacuation. Support is lent to this idea by some other experiments not yet ready for publication. This explanation would also account for the peculiar shape of the adsorption curve in the low vapor pressure region. If some alcohol were held in such pockets, regardless of the low vapor pressure, it would be nearly constant in amount until sufficient liquid became sorbed to open the sealed neck of the pocket, and only after this occurred would it participate in the more general phenomena.

The effect of temperature on the amount of residual alcohol or water throws no definite light on the manner in which it is held, except to indicate that vapor pressure is still active in the phenomenon. In the experiment on the effect of temperature on the amount of residual water, the amount lost on raising the temperature was regained on lowering it. This could not be the case if it were only a matter of increasing the temperature to open some pockets to allow the escape of water trapped in the pockets.

While it cannot be said that the hypothesis is proved by the experimental results, it is claimed that it accords with these results.

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## STUDIES ON LIGNIN AND RELATED COMPOUNDS

XXVII. METHYLATION AND STRUCTURE OF METHANOL LIGNIN (SPRUCE)<sup>1</sup>BY JACK COMPTON<sup>2</sup> AND HAROLD HIBBERT<sup>3</sup>

## Abstract

The composition of spruce methanol lignin prepared by the action of anhydrous methanol-hydrogen chloride on spruce meal was found to vary with the temperature and time of extraction. The reaction mixture contains two products, having methoxyl contents of 21.6 and 24%, respectively. Higher temperatures and longer time of heating favor formation of the latter. Long continued extraction of the crude methanol lignin with ether removed the second product ( $\text{OCH}_3$ , 24%). This showed that this was a true "ether-soluble" fraction, but it was not found possible to isolate the pure methanol lignin ( $\text{OCH}_3$ , 21.6%) by this process. The two substances can be separated either by solvent extraction or, as now shown, by use of 8-10% sodium hydroxide. Methylation of methanol lignin with dimethyl sulphate and alkali gives rise to the formation of new hydroxyl groups, the extent of the changes increasing markedly with rise in temperature of methylation and with increase in concentration of alkali used.

A methanol lignin ( $\text{OCH}_3$ , 22.3%) on repeated methylation yields a methylated lignin containing 37.2% methoxyl. Degradation during methylation is restricted by the use of acetone as solvent and only a slight excess of alkali (5-10%) at 20° C. The results indicate the necessity for caution in the interpretation of data based on methylation experiments involving the use of alkali, and point to the presence of heterocyclic oxygen rings, non-furane in type, as part of the lignin structure. When refluxed for 48 hr. with 65% aqueous methyl alcohol containing 9% sulphuric acid, ether-insoluble methanol lignin ( $\text{OCH}_3$ , 22.3%) yielded a product with methoxyl content 21.3% which decreased to 20.9% when the product was treated for a further 52 hr.

## Introduction

In a previous communication (2) it was shown that crude methanol lignin ( $\text{OCH}_3$ , approximately 23%) prepared from spruce wood-meal by the action of anhydrous methanol-hydrogen chloride solution contains two products, an ether-dioxane soluble product corresponding to true methanol lignin ( $\text{OCH}_3$ , 21.6%) (1) and a second ether-dioxane soluble product ( $\text{OCH}_3$ , 23.6%), the ratio of the two being dependent on the temperature of extraction. Higher temperatures favored the formation of the second derivative.

Their separation can be readily effected (2) by fractionation of the crude methanol lignin first from dioxane-ether solution followed by dioxane-benzene precipitation. It is shown in the experimental part that a similar separation can be effected by the use of 8-10% sodium hydroxide solution at room temperature.

In view of these results and the importance attached to methylation studies as bearing on the structure of lignin, it seemed advisable to investigate the changes, if any, brought about by varying the temperature and quantity of alkali used in the methylation of methanol lignin with dimethyl sulphate, since this procedure is generally regarded as one of the fundamental reactions of all types of lignin. Holmberg and Wintzell (6), using this reagent, methy-

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lated two fractions of alkali lignin, designated " $\alpha$ -" and " $\gamma$ -alkali lignin" with methoxyl contents of 15.4 and 14.6% to give methylated products of 23.4 and 23.2%, respectively. Urban (9) methylated "Willstätter lignin" ( $\text{OCH}_3$ , 15.5%) with dimethyl sulphate and 45% potassium hydroxide at 80-100° C. A methoxyl content of 28.2% was obtained after 15 methylations, while at temperatures below 25° C. the product contained 32.4% methoxyl after two methylations. Heuser and Samuelsen (5), using dimethyl sulphate and 10% sodium hydroxide, methylated lignin sulphonic acid ( $\text{OCH}_3$ , 13.1%) and obtained after five methylations a product with a methoxyl content of 25.4%. Brauns and Hibbert (1) methylated methanol lignin ( $\text{OCH}_3$ , 21.6%) completely with dimethyl sulphate and 30% sodium hydroxide at 56-60° C., the fully methylated product having a methoxyl content of 32.2%. Recently Harris, Sherrard and Mitchell (3), in an investigation on the progressive methylation of Klason lignin (72% sulphuric acid) with dimethyl sulphate and sodium hydroxide, obtained a completely methylated lignin with methoxyl content of 32.2%, in agreement with the value obtained for fully methylated methanol lignin (1).

In the present investigation the methanol lignin used was the ether-dioxane insoluble material ( $\text{OCH}_3$ , 22.3%) obtained by dissolving crude methanol lignin in dioxane and precipitating with ether (2). As already indicated this product is a mixture of two substances with methoxyl contents of 21.5 and 24.5%, respectively. This crude product on methylation with dimethyl sulphate under mild conditions (20-40° C., and using only a slight excess of 7.5 *N* sodium hydroxide) yielded two methylated methanol lignins with methoxyl contents of 32.2% (*A*) and 35.4% (*B*), respectively. More drastic methylation (60° C. and a large excess of alkali) yielded a more highly methylated product (*C*) ( $\text{OCH}_3$ , 37.2%) in addition to (*B*). Repeated treatment of (*A*) and (*B*) with the same methylating reagents showed that: (i) The presence of a large excess of alkali and an increase in temperature brings about partial conversion of (*A*) into (*B*); (ii) A large excess of alkali causes partial conversion of (*B*) into (*C*). Evidently the lignin molecule at higher temperatures and in presence of excess alkali reacts to form new hydroxyl groups capable of methylation. The best methylating conditions for avoiding structural changes are found to be the use of:—(*a*) acetone as solvent; (*b*) a slight excess of alkali (5-10%); and (*c*) a temperature of 20° C., but in view of the above results it is evident that caution is necessary in drawing any conclusions regarding structure based on methylation studies.

Proof that free hydroxyl groups are formed during drastic methylation of methanol lignin resulting in the conversion of  $A \rightarrow B \rightarrow C$  is shown in the fact that neither (*A*) nor (*B*) undergoes acetylation with acetic anhydride in pyridine solution. This indicates probable absence of free hydroxyl groups in these fractions. The efficiency of these reagents for the acetylation of lignin has been proved both by Pringsheim and Magnus (8) and by Heuser and Ackermann (4). The latter authors found that these reagents gave a higher acetyl content than that obtained with any other reagents.

Acetylation of ether-insoluble methanol lignin ( $\text{OCH}_3$ , 21.0%) yields an acetylated lignin ( $\text{OCH}_3$ , 17.6%), whereas the ether-soluble product ( $\text{OCH}_3$ , 24.2%) gives an acetylated product containing  $\text{OCH}_3$ , 20.2%, indicating a different ratio of hydroxyl to methoxyl in each case. Fractionation, after acetylation, of methanol lignin ( $\text{OCH}_3$ , 22.3%) yields an ether-insoluble fraction ( $\text{OCH}_3$ , 18.4%) and an ether-soluble fraction ( $\text{OCH}_3$ , 19.3%). This provides additional evidence that the methanol lignin ( $\text{OCH}_3$ , 22.3%) is a mixture.

The ease with which new hydroxyl groups are formed on methylation would appear to offer supporting evidence for the presence of heterocyclic oxygen rings of a non-furane type.

#### *Action of Acids on Methanol Lignin*

When methanol lignin with a methoxyl content of 22.3% is refluxed with 9% sulphuric acid in aqueous methanol solution (65%) for a period of 24 hr., an ether-insoluble lignin with a methoxyl content of 21.3% is obtained, which value decreases to 20.9% on refluxing for a further 28 hr.

### Experimental

The crude methanol lignin was prepared by the method described previously (2), and was fractionated three times by dioxane-ether precipitation. The ether-soluble fraction was isolated by removal of the excess solvents and precipitation with petroleum ether (2). The results are given in Table I.

Long continued ether extraction of the crude methanol lignin ( $\text{OCH}_3$ , 23.0%) removed one of the products ( $\text{OCH}_3$ , 24%). This showed that the latter was a true "ether-soluble" fraction, but it was not found possible to isolate the pure methanol lignin ( $\text{OCH}_3$ , 21.6%) by this process. As shown previously (2) this can be effected by substituting dioxane-benzene for dioxane-petroleum ether as precipitating medium.

TABLE I  
FRACTIONATION OF CRUDE METHANOL LIGNIN  
( $\text{OCH}_3$ , 23.0%)  
(By use of dioxane-ether)

No. of fractionation	Amount used, gm.	Yield		Methoxyl content	
		Ether insol., gm.	Ether sol., gm.	Ether insol., %	Ether sol., %
1st	55	44.5	7.50	22.9	24.1
2nd	20	17.8	1.05	22.2	24.5
3rd	17.8	17.0	0.55	22.3	24.2

#### *Fractionation of Methanol Lignin with Alkali (8-10%)*

Methanol lignin (1 gm.;  $\text{OCH}_3$ , 21.7%) prepared from spruce wood-meal previously extracted with 5% sodium hydroxide in an atmosphere of nitrogen, was warmed slightly with 8-10% sodium hydroxide (50 cc.), the solution allowed to stand for two hours, and then filtered through a sintered glass funnel. The soluble lignin fraction (7) was isolated by adding the filtrate dropwise to cold 1% hydrochloric acid, filtering, washing, drying, and finally

purifying the lignin by precipitation from dioxane and ether. Yield, 0.86 gm. (86%);  $\text{OCH}_3$ , 21.5%. The insoluble lignin fraction was washed with 1% acetic acid, then with water, dried, dissolved in dioxane and reprecipitated by ether. Yield, 0.14 gm. (14%);  $\text{OCH}_3$ , 23.2%. The above fractionation by means of alkali is possible only with an alkali concentration not less than 8-10%, owing to the complete solubility of the lignin at lower concentrations.

#### METHYLATION OF METHANOL LIGNIN WITH DIMETHYL SULPHATE AND ALKALI

##### *Effect of Temperature and Concentration of Alkali on Methylation of Methanol Lignin ( $\text{OCH}_3$ , 22.3%)*

*Experiment I. Methylation at 20° C. in acetone solution using 7.5 N sodium hydroxide in 5% excess:*—The methanol lignin (2.0 gm.) was dissolved in 2% sodium hydroxide solution (15 cc.), acetone (26 cc.) was added and the solution then treated with five additions each of dimethyl sulphate (5.3 cc.) and 7.5 N sodium hydroxide (7.85 cc.) during one-hour intervals. In each separate addition the reagents were added simultaneously over a period of 15 to 30 min. with rapid stirring which was continued until the end of the hour period, when the next addition was made in the same manner. On completion of the last addition the mixture was stirred for one and one-half hours, and the acetone then removed at 20° C. under diminished pressure. The alkaline mixture, after dilution to 180 cc. with water, was filtered, the residual product ground to a fine powder, thoroughly washed with water, and dried. The crude product was dissolved in anhydrous dioxane (15-20 cc.), centrifuged, filtered and precipitated by pouring into 225 cc. of anhydrous ether. The light, buff-colored product so obtained, after washing thoroughly with anhydrous ether followed by petroleum ether (b.p. 80-90° C.), was finally washed twice with petroleum ether (b.p. 30-50° C.). Yield of ether-insoluble material (Fraction A), 0.95 gm.;  $\text{OCH}_3$ , 32.3%. The ether-dioxane solutions obtained were combined, concentrated and precipitated with petroleum ether. This yielded Fraction B (ether-soluble). Yield, 0.80 gm.;  $\text{OCH}_3$ , 35.3%. Further methylation of either fraction brought about no appreciable change in methoxyl content.

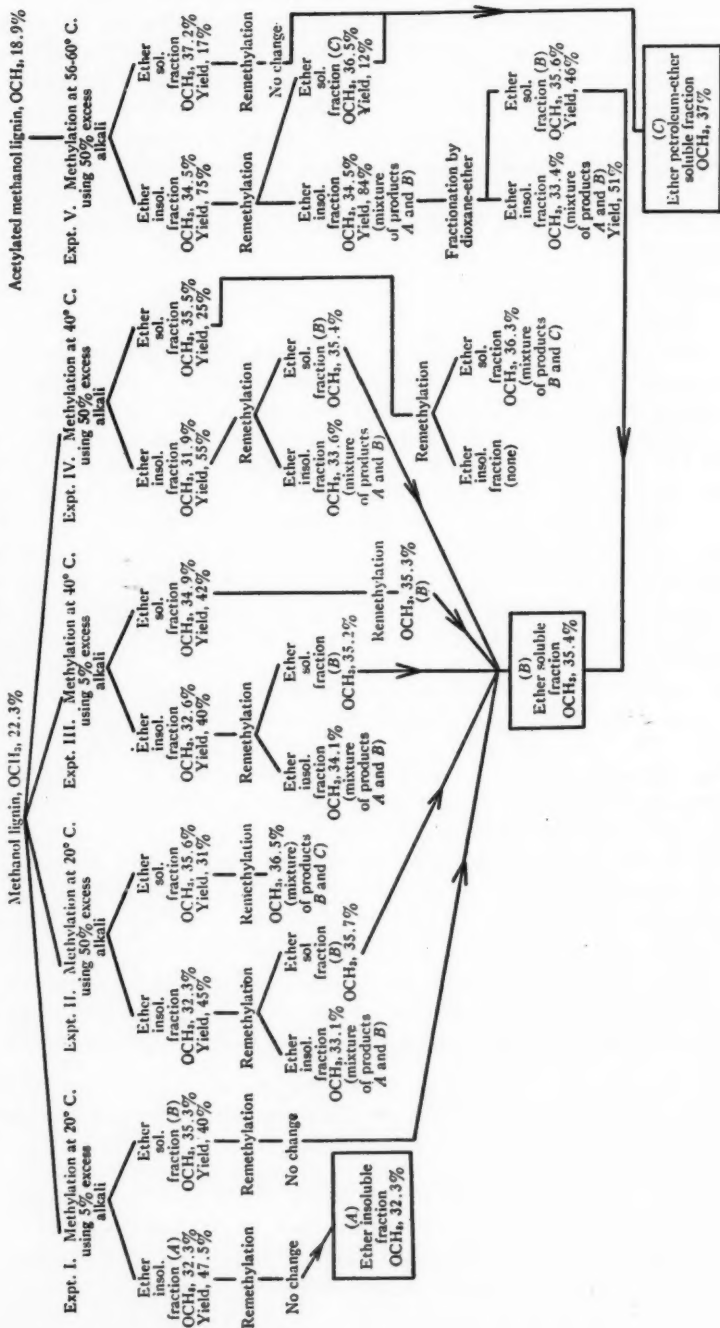
*Experiments II, III, IV and V.* The experimental conditions employed are indicated on the accompanying chart. The remethylations were carried out in the same specific manner for each individual experiment.

*Experiment II.* The results indicate formation of Fraction B from A, while remethylation of Fraction B yields a new product, Fraction C ( $\text{OCH}_3$ , 36.5%).

*Experiment III.* The almost complete conversion of Fraction A into B was indicated.

*Experiment IV.* Partial conversion of Fraction B into a more highly methylated product, Fraction C, was shown.

**METHYLATION OF METHANOL LIGNIN AND ACETYLATED METHANOL LIGNIN IN ACETONE  
USING 7.5 N SODIUM HYDROXIDE SOLUTION**



*Experiment V.* In this experiment, in order to obtain a *maximum* methoxyl value the starting material used was a fully acetylated methanol lignin ( $\text{OCH}_3$ , 18.9%). Fraction A was partially converted into Fraction C with a methoxyl value of 37.2%—the highest yet reported for a methylated lignin.

*Experiment VI.* *Methylation of the ether-soluble fraction of methanol lignin* ( $\text{OCH}_3$ , 24.5%, Table I). The material (1 gm.) was methylated at 20° C. using 5% excess 7.5 N sodium hydroxide solution. The methylated product was purified as described above, except that petroleum ether (b.p. 30-50° C.) was substituted for ether as precipitating agent owing to the ready solubility of the methylated product in the latter. Yield, 0.9 gm.;  $\text{OCH}_3$ , 32.6%. Remethylation gave 0.8 gm. of a more highly methylated product ( $\text{OCH}_3$ , 34.8%).

It follows that the ether-soluble methanol lignin ( $\text{OCH}_3$ , 24.5%) can be methylated directly to the ether-soluble methylated product ( $\text{OCH}_3$ , 35%), since it has been shown (Expt. I) that under these mild conditions the ether-insoluble product ( $\text{OCH}_3$ , 32%) is not converted into ether-soluble material.

#### *Acetylation of Methanol Lignins*

Acetylation experiments provide further evidence that methanol lignin ( $\text{OCH}_3$ , 22.3%) is composed of two methanol lignins ( $\text{OCH}_3$ , 21 and 24% respectively), but the separation is not as clearly defined as in the case of the pure methanol lignins (Expts. I and II).

*Experiment VII.* *Acetylation of methanol lignin* ( $\text{OCH}_3$ , 22.3%, Table I). Methanol lignin (5 gm.) was acetylated in the usual manner with pyridine and acetic anhydride and purified from dioxane-ether. Yield of ether-insoluble product, 2.8 gm.;  $\text{OCH}_3$ , 18.4%. The ether-dioxane solution, after being concentrated to a small volume, was poured, with vigorous stirring, into low-boiling petroleum ether. The precipitated product was thoroughly washed with petroleum ether and dried. Yield of ether-soluble product, 2.5 gm.;  $\text{OCH}_3$ , 19.3%.

*Experiment VIII.* *Acetylation of the ether-insoluble fraction of methanol lignin* ( $\text{OCH}_3$ , 21.3%). Ether-insoluble methanol lignin (1.0 gm.) was acetylated similarly and the reaction product isolated as above. Yield of ether-insoluble acetylated lignin, 0.9 gm.;  $\text{OCH}_3$ , 17.4%. Yield of ether-soluble acetylated lignin, 0.2 gm.;  $\text{OCH}_3$ , 17.9%.

*Experiment IX.* *Acetylation of the ether-soluble fraction of methanol lignin* ( $\text{OCH}_3$ , 24.2%, Table I). Ether-soluble methanol lignin (0.5 gm.) was acetylated as described above. After 48 hr. the acetylated product was precipitated and purified. It was found to be completely soluble in ether. It was therefore necessary to use low-boiling petroleum ether for precipitation. Yield, 0.48 gm.;  $\text{OCH}_3$ , 20.2%.

It may readily be seen that the methoxyl content of the ether-insoluble portion (Expt. VII) agrees approximately with that of the acetylated lignin obtained in Expt. VIII, whereas the methoxyl content of the ether-soluble portion of the former approaches that of the acetylated lignin obtained in this experiment (IX).

*Attempted Acetylation of the Ether-insoluble and Ether-soluble Fully Methylated Methanol Lignins*

*Experiment X. Ether-insoluble methylated lignin* ( $\text{OCH}_3$ , 32.3%). Fully methylated ether-insoluble methanol lignin (0.5 gm.) was acetylated as above. The finely divided, buff-colored powder was purified by addition of the dioxane solution to petroleum ether. Yield, 0.4 gm.;  $\text{OCH}_3$ , 32.4%.

*Experiment XI. Ether-soluble methylated lignin* ( $\text{OCH}_3$ , 35.3%). Fully methylated ether-soluble methanol lignin (0.5 gm.) was acetylated and purified. Yield, 0.45 gm.;  $\text{OCH}_3$ , 35.4%.

In neither Expt. X nor XI was any decrease found in the methoxyl content after acetylation. This indicated the probable absence of free hydroxyl groups.

*Experiment XII. Action of 9% sulphuric acid solution on methanol lignin.* Methanol lignin ( $\text{OCH}_3$ , 22.3%, 2 gm.) was dissolved in warm absolute methanol (130 cc.) and an aqueous 25% sulphuric acid solution (70 cc.) slowly added, during 10 min., in order to avoid precipitation of the lignin. After refluxing for 24 hr., one-half of the solution was removed, filtered hot and the filtrate diluted with cold water (1000 cc.). The lignin was centrifuged, washed with water, then with saturated sodium bicarbonate solution, finally twice with distilled water, again centrifuged and dried in a vacuum desiccator over calcium chloride. It was then dissolved in dioxane solution (25 cc.), centrifuged, filtered, and the lignin precipitated by pouring the solution in a fine stream into dry ether (250 cc.), with vigorous stirring. After washing with ether and then three times with petroleum ether, the product was dried over sulphuric acid. Yield, 0.9 gm.;  $\text{OCH}_3$ , 21.3%.

The remaining half of the original solution was refluxed for a further 28 hr. and the lignin isolated as above. Yield, 0.9 gm.;  $\text{OCH}_3$ , 20.9%.

In both cases the ether-soluble portion was negligible, being less than 0.1 gm.

In a further similar experiment in which 1 gm. of lignin was used, the time of hydrolysis was extended to seven days. The small amount of insoluble product was removed by filtering the hot solution and treating the filtrate as described above. Yield, 0.7 gm.;  $\text{OCH}_3$ , 21.1%.

The lignin portion which separated from the hydrolysis mixture (0.3 gm.) was ground to a fine powder, washed thoroughly with water and dried. It was only slightly soluble in dioxane, but on analysis both dioxane-insoluble and soluble fractions were found to have the same methoxyl value. Dioxane-soluble lignin fraction:  $\text{OCH}_3$ , 17.9%; dioxane-insoluble lignin fraction:  $\text{OCH}_3$ , 17.9%.

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## DERIVATIVES OF SUBSTITUTED SUCCINIC ACIDS

II. THE CONVERSION OF  $\alpha\alpha'$ -DIARYLSUCCINAMIDES INTO DIARYLACETIC ACIDS<sup>1</sup>BY JOHN A. MCRAE,<sup>2</sup> WILLIAM R. CONN<sup>3</sup> AND KENNETH J. PLATT<sup>4</sup>

## Abstract

*p*-Methyl-, *p*-chloro- and *p*-bromodiphenylsuccinamides have been prepared, and their behavior toward alkaline sodium hypobromite under the conditions of the Hofmann reaction has been investigated. The three amides yield as principal products *p*-methyl-, *p*-chloro- and *p*-bromo-diphenylacetic acids. It may be concluded that this behavior is characteristic of  $\alpha\alpha'$ -diarylsuccinamides.

## Introduction

It has been shown recently (8) that  $\alpha\alpha'$ -diphenylsuccinamide is converted into diphenylacetic acid by alkaline sodium hypobromite under the conditions of the Hofmann reaction. To ascertain to what degree this may be considered a general reaction of  $\alpha\alpha'$ -diaryl succinamides, three other amides of the same type, namely  $\alpha$ -phenyl- $\alpha'$ -*p*-tolylsuccinamide,  $\alpha$ -phenyl- $\alpha'$ -*p*-chlorophenylsuccinamide and  $\alpha$ -phenyl- $\alpha'$ -*p*-bromophenylsuccinamide were prepared and their behavior toward alkaline sodium hypobromite was studied. In each case proof was obtained that when these amides are treated first in the cold with alkaline sodium hypobromite and then warmed to 80° C., after the concentration of alkali has been considerably increased, a diarylacetic acid is the principal product of the reaction, although the reaction is always accompanied by evolution of ammonia and benzaldehyde.

Purification of the diarylacetic acids thus formed, to the degree requisite for identification, was rendered difficult by the presence of small amounts of other substances that were retained obstinately. For identification recourse was made to the anilides which, in the first two instances, were compared with authentic specimens of the anilides in question.

These diarylsuccinamides were prepared severally by hydrolysis of the corresponding dinitriles by the methods of Lapworth and McRae (7) for the preparation of diphenylsuccinonitrile and -amide.  $\alpha$ -Phenyl- $\alpha'$ -*p*-tolylsuccinonitrile and  $\alpha$ -phenyl- $\alpha'$ -*p*-chlorophenylsuccinonitrile were prepared by the addition of hydrogen cyanide to the unsaturated nitriles produced by condensing *p*-toluic aldehyde and *p*-chlorobenzaldehyde respectively with phenylacetonitrile. The bromo-compound was prepared by a similar addition of hydrogen cyanide to  $\alpha$ -(*p*-bromophenyl)-cinnamionitrile made from benzaldehyde and *p*-bromophenylacetonitrile.

The anilides of phenyl-*p*-tolylacetic acid and of *p*-chlorodiphenylacetic acid made for comparison were obtained in the usual way from these acids. These

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acids were made according to Gyr's method (5) by the condensation of either the appropriate mandelic acid with benzene or mandelic acid with the appropriate benzene derivative by means of fuming stannic chloride. *p*-Bromodiphenylacetic acid was not obtained in sufficient quantity for use when *p*-bromomandelic acid was used. The required mandelic acids were prepared most readily by Collet's method (3).

Further experiments are in progress to elucidate the nature of the changes involved in these rearrangements, and also to study the effect of substituents of a different character.

### Experimental

*$\alpha$ -Phenyl-*p*-methylcinnamionitrile.* This nitrile was prepared from *p*-tolualdehyde and phenylacetoneitrile according to the method of Bistrzycki and Stelling (1), and was obtained always as an oil even when both the aldehyde and nitrile were distilled freshly under reduced pressure. The oil did not solidify on standing. It was therefore distilled under reduced pressure, b.p. 254° C./44 mm. The distillates from some preparations solidified quickly in part, others remained fluid for months without any separation of the solid phase. The separated solid on recrystallization had the melting point of 61° C.\* given for the substance by Bistrzycki and Stelling. The oily portion reacted with hydrogen cyanide as readily as the recrystallized solid fraction. The oil may be a stereoisomeride. If this is the case it would be expected that the two isomerides would yield isomeric  $\alpha$ -phenyl- $\alpha'$ -*p*-tolylsuccinonitriles on addition with hydrogen cyanide. This was not observed.

*$\alpha$ -Phenyl- $\alpha'$ -*p*-tolylsuccinodinitrile.* This nitrile was prepared as follows. The above-mentioned unsaturated nitrile (40.2 gm.) was dissolved in 800 cc. of hot alcohol. To this boiling solution 28 gm. of potassium cyanide was added in the course of 15 min. This was followed by the gradual addition (15 min.) of 24 gm. of ammonium chloride according to the modification of Brand and Loehr (2). Toward the end of the latter addition the dinitrile began to separate. The mixture was heated under the reflux for an hour. The dinitrile which separated after cooling was collected, washed with alcohol, and hot water. Yield, 39.5 gm., or 88% of the calculated amount. Recrystallized from hot alcohol the substance melted at 195° C. Calcd. for  $C_{17}H_{14}N_2$ : N, 11.38%. Found: N, 11.65%.

*$\alpha$ -Phenyl- $\alpha'$ -*p*-tolylsuccinic diamide.* This was prepared by hydrolyzing the dinitrile by warming 47 gm. of it with 930 cc. of 85% sulphuric acid on the steam bath until solution was effected. On pouring the solution into water the diamide separated. It was digested with cold 3% sodium hydroxide. An almost quantitative yield of crude amide was obtained. For analysis it was recrystallized several times from hot acetic acid in which it is moderately soluble; m.p. 294° C. (corr.) with decomposition. Calcd. for  $C_{17}H_{18}O_2N_2$ : N, 9.93%. Found: N, 10.3%.

\*Unless otherwise stated, melting points are uncorrected.

*$\alpha$ -Phenyl- $\alpha'$ -*p*-tolylsuccinic acid.*  $C_6H_5 \cdot CH(CO_2H) \cdot CH(C_7H_7)CO_2H$ . This acid was obtained in small amounts by acidifying the caustic soda washings of the diamide. It is best recrystallized from alcohol from which it was obtained in colorless platelets, m.p.  $224^\circ C$ . Calcd. for  $C_{17}H_{16}O_4$ : C, 71.83; H, 5.63%. Found: C, 71.80; H, 5.92%.  $C_{17}H_{16}O_4$  requires an equivalent 142. Equivalent found: 141.

*Diethyl  $\alpha$ -phenyl- $\alpha'$ -*p*-tolylsuccinate.* This ester was obtained from the acid in the usual way. On recrystallization it separated from alcohol in thick needles, m.p.  $97^\circ C$ . Calcd. for  $C_{21}H_{24}O_4$ : C, 74.12; H, 7.06%. Found: C, 73.9; H, 7.2%.

*Action of Sodium Hypobromite on  $\alpha$ -Phenyl- $\alpha'$ -*p*-tolylsuccinamide*

The sodium hypobromite solution used was made as previously described (8) from 32 gm. of bromine, 40 gm. of sodium hydroxide and 200 cc. of water. To this solution, maintained at  $-10^\circ C$ . and efficiently stirred, the recrystallized phenyltolylsuccinamide made into a thin paste with water was added during a period of 15 min. The stirring was continued for 30 min., after which the temperature was allowed to rise to  $0^\circ C$ . At this point 24 gm. of sodium hydroxide was added and the mixture heated to  $75-80^\circ C$ . on the water bath. During this heating, ammonia and either benzaldehyde or tolualdehyde or both were released, and at the conclusion of the heating a residue of 4 gm. remained undissolved. Recrystallization showed that this was the unchanged amide. Ether extracted only traces of material. Acidification with hydrochloric acid produced a heavy gummy precipitate. After several methods of purification had been tried the difficultly soluble calcium salt of the acid was obtained by addition of calcium chloride to the solution of the precipitate in ammonia. Gyr (5) had used the calcium salt in purifying his phenyltolylacetic acid. On collecting the calcium salt and reprecipitating the acid, only a slight improvement in quality was shown. The acidic substance was therefore converted into an anilide by rubbing 13 gm. of it with 49 gm. of phosphorus pentachloride, dissolving the crude acid chloride in ligroin and mixing the ligroin extract with 6 gm. of aniline. The anilide which separated was freed from unchanged aniline and recrystallized from dilute alcohol, m.p.  $154-155^\circ C$ . It did not lower the melting point of a sample of genuine phenyl-*p*-tolylacetanilide. Calcd. for  $C_{21}H_{19}ON$ : N, 4.65%. Found: N, 4.89%.

*Phenyl-*p*-tolylacetanilide.*  $C_6H_5(C_7H_7)CH \cdot CONH C_6H_5$

The requisite phenyl-*p*-tolylacetic acid was made according to the directions of Gyr by condensing mandelic acid and toluene by means of fuming stannic chloride. Difficulty was experienced in purifying the acid thoroughly. It was converted into the anilide, and the anilide, recrystallized from hot alcohol, was obtained as fine needles; m.p.  $154-155^\circ C$ . Calcd. for  $C_{21}H_{19}ON$ : C, 83.72; H, 6.30%. Found: C, 83.83; H, 6.04%.

*$\alpha$ -Phenyl- $\alpha'$ -*p*-chlorophenylsuccinodinitrile.*  $\text{ClC}_6\text{H}_4\cdot\text{CH}(\text{CN})\cdot\text{CH}(\text{C}_6\text{H}_5)\text{CN}$

$\alpha$ -Phenyl-*p*-chlorocinnamionitrile was prepared from *p*-chlorobenzaldehyde and phenylacetonitrile according to von Walther and Raetze (9). The method used for the addition of hydrogen cyanide was almost identical with that used for the *p*-methyl derivative. The solutions and proportions used were 20 gm. of this nitrile in 700 cc. of hot alcohol, 14 gm. of potassium cyanide in 40 cc. of water and 12 gm. of ammonium chloride in 40 cc. of water. After heating on the steam bath for three hours under the reflux, 18.5 gm. of the addition compound separated. After several recrystallizations from alcohol the substance melted consistently at 225° C. Calcd. for  $\text{C}_{16}\text{H}_{11}\text{N}_2\text{Cl}$ : N, 10.51; Cl, 13.32%. Found: N, 10.75; Cl, 13.06%.

*$\alpha$ -Phenyl- $\alpha'$ -*p*-chlorophenylsuccinic Diamide.*  $\text{ClC}_6\text{H}_4(\text{CONH}_2)\cdot\text{CH}(\text{C}_6\text{H}_5)\text{CONH}_2$

The above-mentioned nitrile (8 gm.) was hydrolyzed to the diamide by dissolving it in 50 cc. of 90% sulphuric acid on the steam bath and then pouring the solution into water. The amide that separated was washed with caustic soda and recrystallized from glacial acetic acid, m.p. 296° C. (corr.). Calcd. for  $\text{C}_{16}\text{H}_{15}\text{O}_2\text{N}_2\text{Cl}$ : N, 9.26; Cl, 11.74%. Found: N, 9.53; Cl, 11.64%.

*$\alpha$ -Phenyl- $\alpha'$ -*p*-chlorophenylsuccinic Acid*

This was prepared by dissolving the amide (10 gm.) in 50 cc. of 90% sulphuric acid at 100° C., diluting with boiling water until the substance just remained in solution and then heating for four hours at 125° C. under a reflux. The acid obtained by further dilution was recrystallized from alcohol, m.p. 240–241° C. Calcd. for  $\text{C}_{16}\text{H}_{13}\text{O}_4\text{Cl}$ : Cl, 11.75%. Found: Cl, 11.55%.

*The Action of Sodium Hypobromite on *p*-Chlorodiphenylsuccinamide*

The conditions used were identical with those already described for phenyltolylsuccinamide. As before, ammonia and benzaldehyde were evolved during the heating and from 6.7 gm. amide a residue of 1.3 gm. remained undissolved. Acidification produced a gummy precipitate which could be partially purified by recrystallization from hot water. This material was converted into the anilide which on repeated crystallizations from hot alcohol was obtained in long needles melting at 179° C. The substance did not depress the melting point of *p*-chlorodiphenylacetanilide. The identity of this substance with the latter was confirmed further by analysis. Calcd. for  $\text{C}_{20}\text{H}_{16}\text{ONCl}$ : N, 4.36; Cl, 11.04%. Found: N, 4.62; Cl, 10.75%.

**p*-Chlorodiphenylacetanilide*

*p*-Chloromandelic acid was prepared by Collet's method (3) by converting *p*-chloroacetophenone into the  $\omega$ - $\omega$ -dibromoderivative and treating this with 5% potassium hydroxide. The acid was obtained in 39% yield calculated on the dibromo-compound used, and its description agreed with that given by Collet. A mixture of *p*-chloromandelic acid (18 gm.) in 90 cc. of boiling

benzene with 40 gm. of fuming stannic chloride was refluxed for six hours; dilution and extraction with ether gave 18 gm. crude *p*-chlorodiphenylacetic acid. The anilide was made from this acid and recrystallized from alcohol, m.p. 179° C. Calcd. for  $C_{20}H_{16}ONCl$ : N, 4.36%. Found: N, 4.51%.

*$\alpha$ -Phenyl- $\alpha'$ -p-bromophenylsuccinodinitrile*

Instead of combining *p*-bromobenzaldehyde with phenylacetoneitrile, it was found more feasible to combine benzaldehyde with *p*-bromobenzyl cyanide and add hydrogen cyanide to the resulting nitrile. The necessary *p*-bromophenylacetoneitrile was obtained in excellent yield by the action of potassium cyanide on *p*-bromobenzyl chloride instead of the bromide used by Jackson and Lowery (6). It condensed readily with benzaldehyde as described by Frost (4).

The addition of hydrogen cyanide to the  $\alpha$ -bromophenyl-cinnamonitrile took place in almost quantitative yield, when to the nitrile (10 gm.) dissolved in 400 cc. of hot alcohol was added a solution of 7 gm. of potassium cyanide in 20 cc. of water, followed by the gradual addition of 6 gm. of ammonium chloride in 20 cc. of water, and the whole heated for 30 min. The *p*-bromodiphenylsuccinodinitrile which separated was recrystallized from glacial acetic acid, m.p. 213–214° C. (corr.). Calcd. for  $C_{16}H_{11}N_2Br$ : N, 9.00; Br, 25.72%. Found: N, 8.94; Br, 24.9%.

*$\alpha$ -Phenyl- $\alpha'$ -p-bromophenylsuccinic Diamide*

The above-mentioned dinitrile was dissolved in warm 90% sulphuric acid and after a short time the solution was cooled and diluted. The amide separated and after washing it with dilute caustic soda it was recrystallized from glacial acetic acid in which it is moderately soluble when hot, m.p. 300–301°C. (corr.) with decomposition. Calcd. for  $C_{16}H_{13}O_2N_2Br$ : N, 8.07; Br, 23.1%. Found: N, 8.1; Br, 23.5%.

*The Action of Sodium Hypobromite on p-Bromo-diphenylsuccinamide*

Exactly the same conditions were employed as with phenyltolylsuccinamide; 25.9 gm. of *p*-bromodiphenylsuccinamide was used. A considerable amount of amide seemed to remain undissolved in the cold solution, but on heating for three hours at 75–80° C., as previously described, all but 4.2 gm. dissolved. This on recrystallization was identified as unchanged amide and was confirmed by analysis. Found: N, 8.1; Br, 23.4%. The filtrate on standing for some time deposited further crystalline matter but in quantity too small for identification. Recrystallized from acetic acid it melted at 233° C. After removal of this crystalline deposit the filtrate was acidified and a gummy precipitate was thrown down. Various attempts to purify it thoroughly failed. It was therefore converted into the anilide. This was crystallized repeatedly from alcohol and it melted at 177–178° C. The analytical figures agree with those required for *p*-bromodiphenylacetanilide. Calcd. for  $C_{20}H_{16}ONBr$ : C, 65.6; H, 4.37; N, 3.83; Br, 21.9%. Found: C, 65.7; H, 4.64; N, 3.99; Br, 21.8%.

An attempt was made to obtain *p*-bromodiphenyl acetanilide for comparison. *p*-Bromomandelic acid was made from *p*-bromoacetophenone according to the directions of Collet, but the authors were unsuccessful in their efforts to isolate bromodiphenylacetic acid from the product of the action of fuming stannic chloride on this mandelic acid dissolved in boiling benzene.

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